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FIG. 1. — TIMOTHY FERTILIZED WITH LIME AND CHEMICALS.

The crop produced with nitrate of potash, nitrate of soda, acid phosphate, and muriate of potash *with the aid of lime.* Without liming a good stand of timothy could not be secured, and redtop and Rhode Island bent became the dominant grasses. Nitrate of soda, muriate of potash, and acid phosphate have been found to give equally good results.

MANURES AND FERTILIZERS

A TEXT-BOOK FOR COLLEGE STUDENTS AND A WORK OF REFERENCE FOR ALL INTERESTED IN THE SCIENTIFIC ASPECTS OF MODERN FARMING

BY

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PREFACE

The preparation of this volume was undertaken for the purpose of meeting a distinct lack in collegiate agricultural textbooks in the United States. It was hoped to prepare a book reasonably free from extended details, such as are found in certain of the larger foreign works, and likewise to avoid the rather superficial treatment of the subjects which has necessarily characterized many of the books which have been written for the purpose of meeting the earlier requirements of the American agricultural colleges, and the present demands of agricultural high schools. The intent has been to provide in a measure for the needs of the graduate student in agriculture; also for the requirements of students in the agricultural colleges, teachers in agricultural schools, graduates of agricultural schools and colleges, agricultural institute lecturers, and the rapidly increasing number of intelligent men who are daily interesting themselves in the scientific phases of modern farming.

In connection with the treatment of some of the newer and more controversial phases of certain of the topics, authorities have been cited freely, in order that the reader may readily pursue the subjects further, if desired. These citations have been introduced at the bottom of the respective pages, so as to permit of more convenient and ready reference than would be possible if they were placed at the ends of chapters, or at the end of the volume.

Certain points have been referred to repeatedly in dif-

ferent connections, in order that the reader may not have his train of thought interrupted by frequent enforced reference to preceding pages or chapters.

The subject of guano and of human excrement will perhaps be thought to have been treated too fully from the historical standpoint, yet the agricultural teacher is expected to be conversant with such matters, and he can best familiarize himself with them when they are being considered in their manurial relations.

Unusual attention has been paid to the sea-weeds of the Atlantic coast for the reason that they are largely used directly as fertilizers by the farmers, whereas those of the Pacific coast, on account of their larger size, are now being more generally utilized in a commercial way. The consideration of sea-weeds is important, for notwithstanding that they interest directly only a relatively small section of the country, detailed information concerning them is not readily accessible to those students who need it.

In the discussion of the dung of domestic animals, much attention is given to the bacteria and other organisms involved in its decomposition, for the reason that they greatly affect its value under the varying conditions of moisture and aëration.

Not only have organic nitrogenous manures been carefully considered, but also the precautions necessary in determining their relative availability, and the results of such determinations by different investigators.

The subject of nitrates and of ammonium salts has been quite fully treated, especially from the standpoint of their cumulative and indirect effects. The new synthetic nitrogenous fertilizers, calcium cyanamid and calcium nitrate, have also received attention.

More than the customary amount of space has been devoted to the subject of lime and its use, and magnesia, soda, and

manganese have been discussed more fully than in most of the previous works of its kind.

Brief reference is made to the so-called catalytic fertilizers, and to the effect of carbon disulfid, tricresol, toluene, and other substances, certain of which are held to destroy soil amebe and ciliates, and hence to promote unusual bacterial development and ammonification.

Care has been taken to discuss the reasons for many of the conflicting opinions on various subjects, in the belief that those entering upon agricultural research work should be taught to give such matters more careful consideration than is frequently the case.

No apology is offered by the writer for the frequent reference to certain lines of research work at the Rhode Island agricultural experiment station, for the reason that he can speak of these results in a more authoritative way than of work done elsewhere. Furthermore, the work has been, in some respects, of a pioneer character, and has not been duplicated.

In certain of the chapters matter will be found which is of too theoretical a character to meet the needs of the casual reader, and he is requested to pass it over charitably, remembering that the prime object of this work is not to give rule-of-thumb directions, but rather to aid in inculcating such general principles as shall aid in making the student as independent as possible of them, and at the same time furnish a foundation upon which to base his future study of the various relations of fertilizers and manures to soils and crops.

As a matter of convenience to the vast majority of readers, and because of the confusion incident to the use of the names of the elements in place of phosphoric acid, potash, soda, lime, and magnesia which are in common use throughout the civilized world, the old and well-established nomen-

clature has been retained, instead of following the lead of one or two American writers who have seen fit to depart from the universal custom.

Acknowledgments are due to the agricultural experiment station of the Rhode Island State College for all of the illustrations which have been used; likewise to Brooks, Cameron, Dehérain, Fritsch, Griffiths, Hall, Halligan, Heiden, Hilgard, Johnson, King, Murray, Löhnis, A. Mayer, Müntz and Girard, Storer, Van Slyke, Voorhees, Vivian, and others, whose works have been freely consulted; also to Mr. Wilcox, of Mystic, Conn., for details concerning the handling of menhaden, to L. H. Bailey and P. B. Hadley for helpful suggestions, and to my son, Carl O. J. Wheeler, for aid in reading the proofs. A debt of acknowledgment is also recognized to Goessmann, Henneberg, Von Koenen, V. Meyer, Th. Pfeiffer, Tollens, and Stockbridge, whose work and teachings have been of fundamental assistance to the author, as well as a source of lasting inspiration.

H. J. WHEELER.

MAY 12, 1913.

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FERTILIZERS

CHAPTER I

HISTORICAL INTRODUCTION

According to the earlier conception of the term "manure," it meant anything which when applied to the soil will render it more productive. In fact, certain very early English writers referred to the benefits of tillage as a manuring of the land.

The use of the dung of animals, and of chalk, marl, wood-ashes, and certain other substances for increasing the productivity of the soil, was known not only to the early Greeks and Romans but apparently also to the Chinese, whose employment of them for such purposes probably far antedates all human records.

Indeed, Mago, the king of Carthage, in his work on agriculture, which won for him from his enemies, the Romans, the designation "Father of Agriculture," wrote of the value of bird manure, praising especially that of pigeons, and Cato (born 234 B.C.), the first Roman agricultural writer, gave to bird manure the first place.

The manurial effect of various miscellaneous substances, and of certain legumes, was also well recognized not only by the agricultural writers Varro (39 B.C.) and Columella (50 A.D.), but even by the poet Virgil, for the latter, in speaking of ashes and dung, says: —

"But sweet vicissitudes of rest and toil make easy labor, and renew the soil.

"Yet sprinkle sordid ashes all around, and load with fattening dung the fallow ground."

During the dark ages, following the decline of the Roman Empire, practically all records of the use of lime and of other manures are lacking. The knowledge of their value was, however, presumably perpetuated by the studious inmates of the monasteries. Already in the sixteenth century a revival of the knowledge of manuring had begun, as shown by the writings of Bernard Palissy.

Even Jethro Tull, the early English writer who contended that manures are unnecessary if the land is sufficiently tilled, was hardly more radical in his day than a certain recent writer who asserted that the chief function of fertilizers was to improve the physical condition, and later, that it was to render innocuous various toxins of the soil.

1. Chemistry throws new light on the subject of manuring. — A true understanding of the fundamental principles of manuring was made possible only through the aid of chemistry, although more or less general speculation on the subject had long existed, a fact well illustrated by many of the earlier English agricultural writings.

One of the first steps toward a rational understanding of the problems of plant nutrition was the discovery by Priestley, in 1772, that combustion and the respiration of animals deteriorate the air and lessen its volume, but that plants can render it again capable of supporting combustion. This observation, coupled with his discovery of oxygen, led to the recognition of the fact that the bubbles already observed by Bonnet on leaves when they were immersed in water, were chiefly oxygen. It was then shown by Ingenhaus that these phenomena were caused by the action of sunlight, and Sennebier established the fact that the oxygen evolved by plants resulted from the decomposition of the carbon dioxid already taken up from

the air, a fact demonstrated in a quantitative way by De Sassure. The last investigator showed that carbon, associated with the elements of water in the proportions represented by carbohydrates, such as starch and sugar, constitute the chief weight of plants. It was De Sassure, likewise, who recognized nitrogen as a plant constituent, and also the source and value of the ash ingredients. He supposed that the element nitrogen was derived either from the organic constituents of the soil or from ammonia present in the air. The idea that the ash constituents are of special value to the plant was also held by Sir Humphrey Davy.

Several writers, including Thaer, added their contributions to the accumulated knowledge of plant nutrition; but it remained for Boussingault to make the first systematic field experiments. His carefully conducted researches substantiated the accumulation of far more carbon in the plants than could have been derived from the soil. He also showed that more nitrogen was removed in the crops than was supplied in the manure.

2. The views of Liebig. — Notwithstanding the investigations of those who had preceded him, Justus von Liebig soon became the great central agricultural figure, for in 1840 he maintained that if plants are supplied with the small quantity of mineral constituents of the ash, the remainder of their substance can be drawn from the air.

It appears that Liebig was in error concerning the equal importance of the elements of the ash, also as concerns the analysis of the ash being a safe guide in manuring, and in respect to the mode of assimilation of the nitrogen. He also erred as to the possibility of certain elements replacing others which were somewhat similar, as, for example, in the supposed possibility of the complete

replacement of potassium by sodium. It is now of interest to note, however, that the latest researches on this subject by Wilfarth and his co-workers in Germany, and by Wheeler and Hartwell and their co-workers in Rhode Island, uphold the idea of the partial replacement of potassium by sodium, in connection with the whole or a part of some one or more of its functions in the case of at least certain classes of plants. Another question concerning which Liebig was gravely in error was that of the nitrogen supply of plants. He supposed, with others, that the amount of ammonia in the air was much greater than is actually the case, and that this supply was maintained or even augmented with great practical benefit by the ammonia escaping into the air in the course of the fermentation of nitrogenous manures. It was in fact in this way that Liebig supposed that such manures were helpful to plants.

3. **The early work of Lawes and Gilbert.** — Many of the views expounded by Liebig were discredited by John Bennett Lawes (later knighted) of Rothamsted, England, who made a number of experiments on his own account.

When in 1843 John Bennett Lawes associated with himself Dr. Joseph Henry Gilbert, a former student of Liebig's, he took the first great step in systematic agricultural experimentation by the establishment of the Rothamsted experiment farm, upon which they conducted the painstaking researches which have become classic in the annals of agriculture. The subsequent experiments at Rothamsted, in which the American, Pugh (afterwards President of the Pennsylvania State College), was associated, appeared to disprove the supposed assimilation of atmospheric nitrogen which Ville and others believed to have observed. In fact, in the course of the

experiments at Rothamsted in which the soil was sterilized, without thought of the consequences, it was concluded that the gain in nitrogen by legumes was due merely to their great feeding range by virtue of sending their roots so deeply into the soil, — a conclusion which for several years received world-wide acceptance.

4. Assimilation of atmospheric nitrogen by plants. — Notwithstanding the general acceptance of the idea that plants could not assimilate nitrogen directly from the air, the fact was nevertheless shown by Atwater [1] in 1884 in experiments with peas, which were grown in unsterilized soil in pots under such conditions that subsoil was eliminated, and not only all of the nitrogen of the soil, seed, and fertilizers was known, but also the nitrogen in the resulting plants could be determined definitely. Similar experiments were in progress at the same time by Hellriegel and Wilfarth [2] at Bernburg, Germany, which supported fully the conclusions of Atwater. The German investigators went indeed far beyond all who had preceded them and, by a series of experiments extending over a period from 1883 to 1888, established the fact that such assimilation of atmospheric nitrogen is due to the intervention of microörganisms existing in symbiotic relationship in the nodules on the roots of certain legumes. It has since been shown that even a few plants belonging to other families, as, for example, the alder, also assimilate atmospheric nitrogen.

5. Other facts established by Lawes and Gilbert. — The honor nevertheless belongs to Lawes and Gilbert of establishing the dependence of many of the common agricul-

[1] Am. Chem. Jour., 6 (1884–1885), pp. 365–388.

[2] Untersuchungen über die Stickstoffnahrung der Gramineen und Leguminosen, Berlin, 1888.

tural plants on a supply of combined nitrogen, — a fact confirmed by the close relationship of the yields to the quantities of this element added in available form to the soil. It had been held, on the contrary, by Liebig that certain very leafy plants, represented by the common root-crops and clover, can flourish independently of nitrogenous manures (a fact since established for the clovers), and are able to draw their supply from the nitrogen of the air. The field experiments of Lawes and Gilbert also demonstrated the prime importance of potash and phosphoric acid as manures, in contrast with the other constituents of the plant ash. These conclusions were of fundamental importance to agriculture and paved the way for the development of the present enormous fertilizer industry. Other experiments in progress at the same time by Boussingault, Stohmann, and Knop on the growth of plants in various nutrient solutions supplemented the work at Rothamsted and placed the question of plant nutrition on a substantial and scientific basis.

It is an interesting fact that by this work of various investigators in the preceding century there was afforded the first satisfactory explanation of the beneficial effect following the addition to the soil of a whole series of waste nitrogenous materials and substances of other kinds, the utilization of which, in connection with crop production, was recorded in England as early as 1653, and had no doubt been known already for many centuries.

6. The utilization of nitrates and guano. — The importation of nitrate of soda and of Peruvian guano into England for manurial purposes was begun about 1838 and 1840 respectively, although the value of nitrate of potash in connection with the growth of crops was surely known as early as 1669.

7. Employment of ammonium salts. — The ammonium salts were supposedly first employed as manures as a result of the work and writings of De Sassure and Liebig on the utilization of ammonia by plants. Their use by Lawes, however, antedates the appearance of Liebig's memorable paper on the subject in 1840. The systematic trials of a mixture of ammonium chlorid and of ammonium sulfate at the Rothamsted experiment station date from the year 1843.

8. The manufacture and use of superphosphate. — The employment of mineral phosphates, in a limited way, was begun in 1842 when Lawes took out his patent for the manufacture of superphosphate, but they were not to be had in any considerable quantity until three years later, when coprolites were discovered in England.

9. The German potash salts. — It is a noteworthy fact that the common salt manufacturers in certain parts of northern Germany were long troubled by supposedly worthless materials consisting of mixtures of crystalline salts of potassium chlorid, potassium sulfate, and corresponding salts of calcium and magnesium which were associated with some common salt and were found overlying the purer rock-salt deposits. These materials were considered so objectionable and they interfered so seriously with the common salt manufacture that they were given the collective name of "Abraumsalz," which designates something to be taken out of the way. In or about the year 1860, however, the use of these salts for agricultural purposes was begun, — a step which has led to the present enormous output of kainit, muriate of potash, double manure salt (chiefly sulfate of potash and sulfate of magnesia), and of high-grade sulfate of potash, the

world's supply of which practically all comes at present from the German mines.

10. The manufacture of basic slag meal. — Another notable advance in the development of the fertilizer industry resulted from the discovery in 1879 by Thomas and Gilchrist, in England, of a method by which phosphatic iron ore could be effectively freed of its phosphorus in connection with the Bessemer process for the manufacture of steel, and whereby the resulting phosphatic slag was transformed into a valuable fertilizer. It has been stated that the same process was discovered independently by Jacob Reese in the United States. This phosphatic by-product is known under the names "Thomas phosphate," "Thomas meal," "basic slag meal," and the like. The use of this material has already reached enormous proportions in Europe, and it is being exported in considerable quantities to America, Egypt, and elsewhere.

11. New processes for combining atmospheric nitrogen. — Another important advance in the fertilizer industry has been brought about by the recent discovery by Frank and Caro, of Berlin, Germany, of commercially successful methods for the manufacture of calcium cyanamid by the utilization and combination of atmospheric nitrogen through the agency of calcium carbide.

A still further step in advance in connection with the nitrogen fertilizer problem has resulted as a consequence of the discovery of a method by Berkeland and Eyde by which, by the aid of a powerful electric current, atmospheric nitrogen can be combined and united with calcium to form calcium nitrate. In Germany a process has also been devised by which hydrogen and nitrogen gases are made to unite under pressure and form ammonia by the aid of catalytic agents.

12. New catalytic and other fertilizers. — Space will not permit the mention of the many other new processes for the treatment of low-grade crude phosphates, feldspar, and similar materials, in order to increase their availability, and of the series of so-called catalytic fertilizers, such as certain manganese and zinc salts.

Whereas it has seemed with each new discovery that the limit of human invention and accomplishment might have been reached, the recent progress doubtless only foreshadows still greater steps in the immediate future.

CHAPTER II

NIGHT SOIL

The term "night soil" has long been applied to human excrement for the reason that it was often customary, before the introduction of sewers, to remove it from cities and towns during the night.

Human excrement is exceptionally rich in nitrogen and phosphoric acid. This is due not only to the nature of the food consumed, but also to the high degree of digestibility of the non-nitrogenous constituents of the diet, as compared with the coarser feeds consumed by the domestic animals. By the fermentation of the excrement great losses of nitrogen may result.

13. Conservation of night soil now less necessary. — Owing to the rapid consumption of the natural supply of nitrate of soda, the fear was expressed quite recently that through the drain upon the land occasioned by the great numbers of people living in cities, and the almost universal waste of their excrement in the sewage, a nitrogen famine might result. Fortunately, this fear has been dispelled by the more recent discovery of economical methods for the production of calcium cyanamid, calcium nitrate, and ammonia from the inexhaustible supplies of limestone, atmospheric nitrogen, and hydrogen.

Danger to health. — One of the great objections to the use of human excrement as a manure is that it is often a

great source of danger, on account of its being a ready medium for the conveyance of the organisms which cause various types of human disease. The necessity of providing a safe place for the deposition of human excreta at a distance from the abiding place of man, is even set forth in the Bible (Deuteronomy 23, verses 12 and 13).

14. Amount of urine produced per person. — According to Heiden, a single individual produces in the course of the year about 1000 pounds of excrement, having a usual fertilizing value of from two to three dollars.

It was found by Lecanu, in experiments with sixteen persons of different ages and sexes, that the excretion of urine, per twenty-four hours, ranged from 525 to 2271 grams. In experiments conducted on himself, Lehmann found, in a fourteen-day test with a mixed diet, that the daily excretion of urine amounted to from 879 to 1384 grams; and in the course of a twelve-day vegetable diet, it fell to from 720 to 1212 grams. Based upon these and other data, it is probably safe to estimate the average daily excretion of urine, per capita, at about 1200 grams (about 4.2 pounds).

The solid matter in human urine has been found, based upon the work of several investigators, to range from about 34.5 to 87.4 grams per day, though it is said to vary with the different nationalities. This variation may, however, be due to temperature and other climatic conditions, rather than to constitutional differences.

15. Chemical composition of human urine. — The following percentages, given by Lehmann, represent the relative quantities of some of the more important constituents of human urine: —

	Urea	Uric Acid	Extractive Substances and Salts
With a mixed diet	32.5	1.18	12.8
With an animal diet	53.2	1.48	7.3
With a vegetable diet	22.5	1.02	19.2
With a nitrogen-free diet . . .	15.4	0.74	17.1

It appears therefore that the urine varies greatly in composition, as well as in amount, according to the diet of the individual.

It has been found that the percentage of nitrogen in the urine of children eight months old is about 0.15; in that of men 21 years old, 1.02, and in the urine of men of 46 years, 1.57 to 1.84. Based upon an average of 1200 grams of urine per twenty-four hours per individual, the average daily excretion of nitrogen in the urine would amount to 13.36 grams.

The quantity of non-combustible salts is least in the urine of children, followed in turn by the urine of women, aged people, and men. The variations, however, in individual cases, and within these groups are very great. The chief constituents of the ash of urine, named in order, are chlorin, soda, potash, phosphoric acid, sulfuric acid, lime, magnesia, and iron oxid. Slight amounts of insoluble matter make up the remainder.

16. The amount of solid excrement per individual. — The average quantity of solid excrement, per day, as found by Lawes and Gilbert, for boys under sixteen years of age, was about 108 grams; for men between 16 and 50 years, it was about 152 grams; and for men over 50 years of age, about 226 grams. The dry substance ranged

from 27.4 to 42.3 per cent; it was found to be greatest in the case of old men. The amount of nitrogen present in the average daily excretion of the solid excrement of boys was 2.34 grams, of men 1.94 grams, and of old men, 0.321 gram. The quantities of ash were 3.69, 4.23, and 8.32 grams, respectively. In the ash the phosphoric acid has been found to range from about 31 to 43 per cent, the potash from about 6 to 21 per cent, lime from about 17 to 27 per cent, and magnesia from about 10.5 to 15.5 per cent.

Heiden gives the following as the average quantity of both solid and liquid excrement per person daily: —

	Solid Grams	Liquid Grams	Total Grams
Total quantity	133.0	1200.0	1333.0
Solid matter	30.3	64.0	94.0
Organic matter	25.9	50.0	75.5
Nitrogen (in organic matter)	2.1	12.1	14.2
Ash	4.5	13.0	17.5
Phosphoric acid (in ash)	1.6	1.8	3.4
Potash (in ash)	0.7	2.2	3.0

17. Former methods of disposal in Europe were bad. — In Europe, generally, the conditions connected with the disposal of human excrement were, until a comparatively recent period, extremely bad, and even after the construction of sewers emptying into the most accessible streams, the situation became highly dangerous to the public health. In England this led to the appointment of a special commission to inquire into, and report concerning, the matter. As a result of this and of similar agitation in

other lands, the present efficient septic tank and combined precipitation and filtration systems have been evolved.

18. Orientals conserve human excrement carefully. — Japan and China have thus far led the world in the systematic saving and use of human excrement for agricultural purposes. It has been possible thereby in the past, not only to maintain the enormous population of those countries, which is five to six times as dense as that of certain of the chief countries of Europe, but they have also been able, since the opening of their ports, to export to other countries considerable amounts of human food. In view of the practical economies of the Oriental nations in this respect; and in view of the fact that the world seemed to be facing a future nitrogen famine, many systems for the preservation of human excrement have been devised from time to time. Owing, however, to the present methods of transforming the inexhaustible nitrogen supply of the air into available plant food in an economical way, it is unnecessary to devote space here to their description, from the standpoint of the conservation of nitrogen, more than by way of the briefest historical reference.

19. The conservation of human excrement in Paris. — The first police ordinance of the city of Paris, relating to the disposition of human excrement in a secret vault or similar place in each house, dates from 1348, but it was not until 1583 that a penalty for such an omission was provided. Regulations for the construction of such receptacles were made in 1809 by a decree of Napoleon, which was renewed in 1819.

From 1781 to 1849 the human excrement of the city of Paris was deposited in an abandoned suburban quarry from which source the offensive odors penetrated a con-

siderable portion of the city. As a result, provision was finally made for its disinfection and for effecting a separation of the liquid and solid excrement. The former was then conducted into cisterns just outside of the city, from whence it was pumped to a more distant point, to which the solid excrement was at once conveyed by boat. Here the mass was left in open beds for several months. After the liquid portion had been clarified, it was utilized for the manufacture of ammonia. The remaining solid matter, after drying for a time in the beds, was further dried in the field, and then sold under the name of "poudrette." A part of the excrement was, however, still turned into the canals and found its way into the river Seine.

Still later, after it was found that the method of disposal just described was not economical, the Seine became the receptacle for the entire mass of this material. The conditions which arose in consequence were so serious that a commission was appointed to investigate the entire subject, and, as a result, a modern filtration system was adopted.

In the meantime in Lyons, in the south of France, and here and there in England, attention had already been given to saving some of the human excrement for agricultural purposes.

The history of the situation in Paris is typical in many respects of the steps taken in other European cities, which have finally resulted in the present methods of municipal sewage disposal.

20. "Poudrette" from human excrement. — One of the products sold under the name of "poudrette" is prepared by the Liernur process, which consists in adding to the excrement sufficient sulfuric acid to bind the ammonia, after which the mass is evaporated in a vacuum until it reaches such a consistency that it can be completely

dried by other means and finally reduced to a powder. It happened, unfortunately, that the tendency to introduce foreign material, by way of adulteration, brought such poudrette into more or less general ill repute.

21. Treatment of excrement with burned lime. — Another but more wasteful process for the utilization of human excrement consists in treating it with burned lime. This method is said to have been first proposed by Payen and then by A. Müller, and upon it is based the system of Mosselmann and Müller-Schür. By this process the ammonia which has been formed previously in the mass is lost. It is therefore important that the excrement be treated in as fresh a state as possible. Mosselmann used two parts by weight of burned lime to one of moist excrement, and the final volume amounted to two and one-half times that of the lime employed. In this process 100 parts by weight of lime volatilize about 25 parts of water and bind chemically and mechanically about 50 parts more, thus producing a product which is so dry that it can be readily handled and transported, and the heat generated is sufficient to destroy pathogenic organisms. Such a system was in use recently in connection with the disposal of the excrement from tenement houses in certain manufacturing villages in Rhode Island, and the following is the composition of the product thus secured: —

	Per Cent
Calcium oxid	11.28
Potassium oxid	0.09
Phosphoric acid	0.91
Nitrogen	0.43

One great objection to the material prepared by this process is that it is so excessively rich in lime that if it

were applied regularly in sufficient quantities to supply the soil adequately with the other fertilizer ingredients, it would result in liming to excess. It may, however, be used frequently, for a time, on soils originally quite acid or, more infrequently, on those only moderately in need of liming. To meet this objection in part, basic slag meal, potash salts, and other chemicals have sometimes been incorporated with it before placing it on the market.

22. The "A. B. C." and other methods of conservation. — In the absence of burned lime, alum, blood, and clay have been added to the excrement, after which the solid matter is dried, ground, and marketed under the name of "native guano." This process takes its name "A. B. C." from the first letter of the name of each of the materials added to the excrement. A large number of other methods for the disposal of human excrement, by its transformation into poudrette, have been proposed from time to time. Some of these, like that of Teuthorn, involve evaporation and drying of the mass by natural means, whereas that of Thon was based upon evaporation of the water by means of artificial heat. The product as prepared by Thon at Stuttgart had the following composition: —

	Per Cent
Nitrogen	4.5– 6.0
Phosphoric acid	10.0–12.0
Potash	1.5– 3.0

In connection with the many other processes which have been employed for the same purpose at various times, practically every conceivable absorbent and conserving material has been used.

23. The novel method of Sindermann. — Among all of the methods proposed for the disposal of human excrement, perhaps the most novel is that of A. Sindermann,

which was adopted in connection with a hotel in Breslau, Germany. The excreta in this case were placed in a retort, where they were not only dried, but also subjected to dry distillation, in the course of which there were produced illuminating gas, carbon dioxid, tar, oil, and ammonia. The valuable products were saved, as in the manufacture of gas from coal; the gas, after the removal of the carbon dioxid and subjection to other purification, was used for illuminating purposes in the hotel. The resulting ash, with a content of 5.57 per cent of water, was found to contain 6.5 per cent of lime, 3 per cent of magnesia, 5.5 per cent of potash, and 8.6 per cent of phosphoric acid.

24. Repeated use encourages undue leaf growth. — In general, it may be said that the continued use of considerable quantities of human excrement on land leads to unusual leaf growth, and, in the case of grass land, causes the lodging and consequent molding of some of the crop. Its excessive use also results in delaying the fruiting of other crops. The economical utilization of such material depends, therefore, upon limiting the amount used to that required to furnish the needed nitrogen, and on its being supplemented by proper amounts of potash and phosphoric acid.

CHAPTER III

THE DUNG OF FARM ANIMALS AND ITS PRESERVATION

The term "farm manure" covers properly the dung of all the domestic animals kept on the farm, including the customary litter, night soil, peat, muck, leaf mold, other vegetable refuse, and composts. Barn-yard manure, as usually understood, relates to the dung of neat cattle with the usual litter. Stable manure is a term at present more commonly applied to the dung and litter from horse stables.

25. Influence of feed and age of animal on dung. — It may be stated that in general the dung of mature animals is of greater value than that of those which are making rapid growth; similarly, the dung of cows not with calf and especially of those not producing milk, is richer than that of animals bearing their young or which are yielding large volumes of milk. The reasons for this are sufficiently obvious. It is assumed of course in such instances that the feeds are of the same general character. The dung of animals fed chiefly on grain, milk, and other similar materials is richer than that of those which subsist chiefly on coarse feeds, since it contains much more nitrogen, the most costly of all the manurial ingredients.

26. Influence of litter on manure. — The value of dung, as it has to be dealt with in a practical way, is very greatly affected by the kind and quantity of litter or

absorbents employed in the stables or yards. For example, the manurial value of cacao refuse or of peat or muck is of itself far greater than that of such materials as sawdust, shavings, and cotton waste, which are exceedingly poor in nitrogen and in other less valuable manurial ingredients.

27. Collecting and caring for dung. — The method of collecting and of caring for the dung of the farm animals may affect its value greatly. If it is thrown out under the eaves of the stable, as was once a too common custom in the United States, most of the liquid or more valuable portion, representing about four-fifths of its total value, is likely to be carried away in the rain water. If, on the other hand, horse manure is allowed to lie in an undisturbed pile in a barn cellar and to undergo fermentation until it reaches a "fire-fanged" condition, great loss of nitrogen inevitably results. Serious, though less extensive losses of nitrogen occur through volatilization of ammonia either in the stable, cellar, or storage shed, on account of the failure to use chemical agents for its retention; but more particularly from leaving it either in small heaps or spread upon the surface of the ground for some time before the land is plowed.

28. Horse manure. — Because of the fact that the horse has but one stomach, and hence does not ruminate, it is not as well able as the sheep and cow to completely disintegrate and digest coarse feeds. On this account, and due to the presence of large amounts of fibrous material, horse manure is especially open and porous in character.

Subject to ready fermentation. — On account of the less complete destruction of the organic compounds of the hay and grain in the course of the process of digestion, horse

manure furnishes abundant organic food for the many microörganisms which promote decay, and hence it is especially subject to fermentations of various kinds. This fact is taken advantage of by its employment for the evolution of heat in greenhouses and cold-frames. Owing to its loose physical character, horse manure is often mixed with cow manure, for certain purposes, with distinct advantage to each.

The solid portion. — The solid excrement of horses consists chiefly of the undigested portions of the feed, associated with bacteria, minute quantities of biliary matter, and epithelial tissue, arising from the normal destruction of intestinal surfaces. The average composition of the solid manure is as follows: nitrogen 0.55 per cent, phosphoric acid 0.30 per cent, and potash 0.40 per cent.

The liquid portion. — The liquid excrement contains soluble phosphates, potash salts, and the organic metabolic products of the animal, such as urea, traces of creatinin ($C_4H_7N_3O$), and, in the case of horses at rest, small quantities of hippuric acid. The urine of horses is more concentrated than that of the bovine species, and it constitutes about one-fourth of the weight of the total excrement. The following represents the average analysis of the liquid manure: nitrogen 1.35 per cent, phosphoric acid a trace, potash 1.25 per cent. After being added to the solid portion the mixture has the following composition: nitrogen 0.7 per cent, phosphoric acid 0.25 per cent, and potash 0.55 per cent.

Storage, and the use of litter. — Usually a greater percentage of litter (bedding) is used for horses than for cows, on which account the manure as a whole is often of a more strawy character. The value of the manure is usually considered greater if straw or leaves are used for bedding

than if either shavings or sawdust is employed. This is, however, more likely to be true if the shavings are made from the wood of pine and of certain other coniferous trees. Experiments are nevertheless on record, showing that cow manure has been found to be equally as valuable with sawdust litter as with a litter of straw or chopped corn stalks, when used for roses, carnations, chrysanthemums, and sweet peas. For certain reasons, manure without litter was preferred in special cases.[1]

If horse manure is to be stored before its application to the soil, it should be compacted at once as completely as possible, and especial care should be taken to keep it moist.

Amount of manure produced per animal. — It is estimated that every 100 pounds of dry matter in the feed of a horse will produce about 210 pounds of manure, containing about 77.5 per cent of moisture. Allowing in addition 6.5 pounds of bedding per day per horse, and allowing also for the manure usually voided outside of the stall, there would be available for use about five and one-fourth to six and one-third tons of manure per horse per annum.

29. Cow manure. — The manure of neat cattle, owing to their habit of ruminating and to the comparatively complete digestion afforded by their four stomachs, is far more compact than horse manure, and hence for many purposes is improved by an admixture of the latter. Nevertheless, in the preparation of soil for rose culture under glass, and for certain other greenhouse, garden, and farm purposes it is preferred, by many, unmixed with horse manure.

Chemical composition. — The chemical composition of cow manure is much like that of horse manure, though

[1] Pub. Int. Agr. Inst. (Rome), Ottawa Branch, Bul. 2, No. 6, July, 1912.

it is less concentrated, and it contains about one per cent of hippuric acid ($C_9H_9NO_3$).

Quantity voided per cow. — The quantity of manure voided by the cow is much greater than that produced by the horse, which compensates in a measure for the more dilute character of the liquid portion, when considering the total value of the yearly product of each. The quantity of manure excreted daily per cow, inclusive of the customary quantity of absorbents, is from twenty-five to thirty pounds greater than that produced by the horse. One pound of dry matter in the feed will furnish about 3.84 pounds of manure. To this must be added the litter in order to show the total amount of manure produced per animal. An average cow, if properly fed, will excrete approximately 65 pounds of manure per day, about 25 per cent of which is represented by the liquid portion. It is obvious that there will be wide individual variations from these figures, dependent upon the weight of the cow and upon the character and digestibility of her feed.

Proportion of the nitrogen voided. — About one-fourth of the nitrogen of the feed is appropriated by the cow for the manufacture of her milk product, and to replace hair and other waste, leaving another and less valuable fourth in the solid excrement, and one-half in the liquid manure.

30. Sheep manure. — The value of the manure produced by a single sheep in a year is small. The manure always contains less water than that of other domestic animals, the average content being about 74 per cent. Sheep manure is especially prized by many florists for use in greenhouses, due, doubtless, in part to its improvement of the physical character of the soil; it is also much sought in some localities for application to lawns and for the production of certain garden crops. Owing to the low water

content of sheep manure, it is liable to ferment easily and to lose some of its nitrogen as ammonia. The average composition of the mixed solid and liquid manure is as follows: nitrogen 0.95 per cent, phosphoric acid 0.35 per cent, and potash 1.00 per cent.

Amount of manure produced by sheep. — At the Cornell agricultural experiment station, it was found that three sheep fed for thirty-three and two-thirds days produced a total of 723 pounds of solid and liquid excrement. The average of a large number of German experiments shows that for 100 pounds of dry matter of the feed there are recovered 48.4 pounds of dry matter in the excrement. In general, the multiplication of the dry matter of the feed by 1.88 and the addition of the litter will give approximately the amount of manure. On the basis of 73 per cent of water in sheep manure, 100 pounds of dry matter of the feed would produce 183 pounds of manure; or, in other words, a sheep weighing about 60 pounds would consume about 2 pounds of dry matter daily, which, with an amount of litter such as is often used, would amount to about 1500 pounds of manure per year.

31. Hog manure. — As a rule, hog manure is of less interest than that of other domestic animals, for the reason that a large portion of it is often voided in the field. It varies also so widely in composition, owing to the diversified character of the food consumed, that one cannot give a value to it within very definite limits. Assuming the food to be the same, hog manure will not vary widely from the composition of the manure of other animals. The average of a considerable number of experiments shows that for every 100 pounds of dry matter in the feed consumed there will be produced about 237 pounds of manure. The liquid manure of hogs which have been well fed often

contains as much as 2 per cent of nitrogen. The solid excrement of hogs is very wet and decomposes less readily than that of horses and of sheep.

A hog will void on the average from 12 to 15 pounds of manure per day, which is equal to from two to three tons per year.

There seems to have existed among farmers a certain prejudice against the use of hog manure for certain crops, although there seems to be no satisfactory experimental basis at this time for definite statements on this point.

32. Hen and pigeon manure. — The manure of hens and pigeons differs materially from that of the more common farm animals, by reason of the fact that the excreta are voided in one portion, rather than separately in solid and liquid form.

Chemical composition. — A number of analyses of fresh hen manure show the range in nitrogen content to be from 0.56 to 1.38 per cent; in phosphoric acid, from 0.35 to 1 per cent, with the majority ranging from about 0.47 to 0.92 per cent; and the range in potash is from 0.18 to 0.45 per cent, though the more common limits are between 0.25 and 0.4 per cent.

Air-dry hen manure contains from 1.82 to 2.13 per cent of nitrogen, from 0.85 to 2.21 per cent of phosphoric acid, and from 0.35 to 1.11 per cent of potash. It is not an ideally balanced manure for all purposes, and can usually be supplemented profitably by the addition of a liberal amount of acid phosphate and by a moderate quantity of muriate of potash or of kainit. When so employed, the results from its use, even in much smaller quantities than otherwise, are excellent.

Both superior in their action. — The superior action of pigeon and hen manure may readily be attributed in part

to the fact that the liquid and solid manure are voided together, in consequence of which the metabolized nitrogen is less likely to suffer loss by leaching than in the case of most other manures. Furthermore, it very quickly undergoes nitrification after its application to the soil. These manures are naturally richer in nitrogen and in other fertilizer ingredients than certain coarser manures, owing to the more concentrated character of the feeds consumed. In view of the foregoing circumstance, these manures contain less of the various organic materials which characterize especially horse manure, and hence furnish a smaller supply of the organic foods for the organisms which are especially concerned in denitrification and the liberation of nitrogen in a free state.

Both manures need supplementing. — The adaptability of hen and pigeon manure to general trucking and gardening purposes would often be much increased, and the ammonia better conserved, if 12 to 15 pounds of acid phosphate and 18 to 20 pounds of kainit, or 4 to 5 pounds of muriate of potash were added to every 100 pounds of the fresh manure. It might be still further improved by adding to each 100 pounds, 5 to 10 pounds of gypsum, or land plaster.

33. Amounts of litter used as absorbents. — The quantity of litter which should be used is not only dependent upon the class of farm animals concerned, but also upon the character of the food consumed; since watery foods and those containing a large amount of nitrogen cause an increased flow of urine. It is generally desirable to employ sufficient litter to keep the animals clean, by insuring the absorption of the liquid manure. To this end it has been recommended that the amount for cattle per day should be 9 pounds, for horses 6.5 pounds, and

for sheep three-fifths pound. Stated in another way, the litter should be equal, approximately, to one-third of the dry matter consumed.

34. Comparative absorbent power of litters for water and ammonia. — The ability of the litter to absorb liquid may differ widely from its capacity to hold ammonia, as shown in the following table:—

Kinds of Material	Water Retained by 100 Pounds of Material after 24 Hours Pounds	Ammonia Absorbed by 100 Pounds of Different Materials Pounds
Wheat straw	220	0.17
Oat straw	285	—[1]
Pea straw	280	—
Partially decomposed oak leaves	162	—
Dead leaves	200	—
Peat	600	1.10
Needles of coniferous trees	175	—
Sawdust	435	0.05
Spent tan	450	—
Air-dried humous soils	50	0.66
Mosses and forest leaves	275	—
Peat moss	—	0.86
Sand	25	—

[1] Not determined.

It will be seen that in proportion to the amount of liquid held, air-dried humous soil is a most efficient absorber of ammonia. This is no doubt due in part to a chemical union of the ammonia with organic acids present in the humus, as well as to a similar union with zeolites and possibly other complex silicates of the mineral portion of the

soil. As absorbents of ammonia, peat, peat moss, and humous soil take the first rank.

In so far as concerns ability to take up and hold water, peat is superior to all of the other absorbents.

Both loam and peat may be used effectively in bedding, as supplements to, and economizers of, straw.

In a series of tests made with cotton waste at the experiment station of the Rhode Island State College, it was found that 100 pounds of a dyed and quite clean sample absorbed 435 pounds of water. The same quantity of an undyed lot of similar character absorbed 550 pounds, and two other lots, which contained considerable quantities of fine foreign matter, absorbed but 267 and 231 pounds of water, respectively.

35. The degree of conservation effected by litters. — It was found by Müntz and Girard that where the loss of nitrogen from the manure of cows amounted to 59 per cent without the use of litter, its addition reduced the losses to 50 per cent and 44 per cent. Where excessive quantities of litter were employed, the losses were nevertheless 41 per cent. In their study of the relative efficiency of straw and peat moss, in the preservation of horse dung, it was found that the loss of nitrogen, when straw was employed, was 58 per cent; whereas with peat moss it was but 44 per cent. Similar experiments with straw, in the preservation of sheep manure, showed a loss of 50 per cent of the nitrogen, whereas by the substitution of a litter of earth, the loss was reduced below 26 per cent.

36. Losses of manure lessened by packing and trampling. — Since very early times it has been a common practice to pack horse manure, in order to prevent its rapid fermentation and consequent "fire-fanging," which, if unchecked, results in the loss of most of its nitrogen.

Similar packing in the case of other manures also minimizes the loss of nitrogen, as has been shown by numerous experiments.

The compacting of horse manure and cow manure is often accomplished in this country and in Europe by confining swine or other farm animals within the inclosure where the manure is stored.

In Europe it is a common practice to place the farm animals in deep stalls, having cemented sides and bottoms. They are then littered generously and allowed to remain in the stalls for several months on the accumulations of manure and litter. When such methods are practiced, the usual losses of nitrogen range from about 13 to 18 per cent. This loss is occasioned not only through the direct volatilization of ammonia, but by the transformation of considerable quantities of the more readily soluble and available nitrogen into less available forms, through bacterial agencies. The change of available nitrogen into more inert forms also accompanies the process of denitrification; whereby also much of the nitrogen of nitrates may, under certain conditions, be liberated as gaseous nitrogen. The nitrogen thus rendered inert is transformed into what is commonly classified as humous nitrogen, a direct product in this case of the destruction of the organisms of which it became at first a constituent part.

It is cited by Hall that in experiments made by Russell and Goodwin, 43.83 pounds of digestible nitrogen were fed, and but 3.07 pounds of it were retained by the animal which consumed the feed containing it. The remainder, represented by 40.76 pounds, was voided as urea. Upon subsequent examination of the dung, it was found, however, that but 28.6 pounds of nitrogen remained in the shape of ammonia and amids, and that, aside from a direct

loss of 7.38 pounds of nitrogen, 4.78 pounds had been converted, during the fermentation, into proteins and other insoluble compounds.

It has been found by Maercker and Schneidewind, in experiments with steers, that manure properly trampled suffers an average loss of about 15 per cent of its nitrogen, but that the loss will readily rise to from 30 to 40 per cent, if the manure is thrown out into piles daily, or at quite frequent intervals.

The richer the manure in soluble or immediately available nitrogen, the greater is likely to be the percentage loss of nitrogen during the making and storage, and hence such manures should receive most careful attention.

37. Soil a powerful absorbent of ammonia. — In experiments performed by Müntz and Girard it was found that uncovered cow manure suffered a loss of 142 milligrams of ammonia, but that, under otherwise like conditions, when covered with soil to a depth of about three-quarters of an inch (2 cm.) the loss was but 10 milligrams. Similarly the loss of ammonia from uncovered sheep manure amounted to 1642 milligrams, but with a covering of soil like that used with the cow manure, the loss was but 128 milligrams. In experiments with air-dried sandy soil, as a litter for sheep, the loss of nitrogen amounted to but 25.7 per cent of that consumed in the feed, as compared with a loss of 50.2 per cent, when straw was substituted for the soil.

How the soil acts in retaining ammonia. — The retention of ammonia by soil is probably due chiefly to three causes. The first and least important is its direct absorption and retention by the moisture held on the surface of the soil particles; the second is its combination with organic acids, arising in the course of the decomposition of

vegetable débris; and the third is its entering into combination with zeolites or similar complex silicates. In this form it lends itself, nevertheless, very readily to subsequent nitrification. It is also known that dry soil will absorb gases of various kinds by condensation on the surface of the particles, analogous to the condensation of oxygen on platinum black, and of nitrogen on porous copper oxid.

38. Müntz and Girard's results on the absorption of ammonia. — The following data from Müntz and Girard show the relative amounts of ammonia absorbed by soil and other substances: —

AMMONIA ABSORBED, PER KILOGRAM OF DRY MATTER, BY DIFFERENT SORTS OF MATERIAL

	GRAMS
Wheat straw	1.70
Pine sawdust	0.46
Mossy peat from Holland	8.63
Powdered peat	11.03
Siliceous earth	0.66
Calcareous earth	1.80
Argillaceous forest soil	2.24
Garden soil	5.38
Peaty soil	6.60

It will be observed that the highest absorptive power is possessed by peat and by soils rich in humus, whereas siliceous soil and sawdust both stand low in the list. Attention has been called by Hilgard to the remarkable absorptive power, both for ammonia and carbon dioxid, possessed by certain highly ferruginous soils of Hawaii, which appear to exceed all others in this respect. These soils were found to contain as much as 40 per cent of ferric oxid accompanied by 3.5 per cent of humus.

39. The action of gypsum as a preservative of manures. — Gypsum, or land plaster, has long been considered one of the most important chemical substances for use in the preservation of animal manures. Its value is based upon its ability to transform the unstable ammonium carbonate into ammonium sulfate, whereby its volatilization is prevented. This reaction is expressed by the following equation: —

$$(NH_4)_2CO_3 + CaSO_4 \cdot 2H_2O = (NH_4)_2SO_4 + CaCO_3 + 2H_2O$$

ammonium carbonate — gypsum — ammonium sulfate — calcium carbonate — water

It requires about 400 parts of water to dissolve 1 part of gypsum, although its solubility may be somewhat greater in the liquid manure. In order to be effective, the manure pile must be kept quite moist in order that the solution and transformation, and the consequent fixation, may take place promptly and efficiently.

40. Reasons for using gypsum in excess. — In consequence of the fact that the reverse reaction to that mentioned above is possible, far more than the theoretical quantity of gypsum must be used in order to insure the fixation of even the chief part of the ammonia. Furthermore, if the material loses its moisture, some of the ammonia of the ammonium sulfate will be changed again into ammonium carbonate. Theoretically, 10 to 12 pounds of gypsum should be used per ton of dung, but in actual practice from 100 to 120 pounds should be employed. Another reason for the employment of more than the theoretical quantity of gypsum is that potassium carbonate and sodium carbonate are present in the urine, which also react with gypsum in the same manner as the ammonium carbonate. Still another reason for using a generous

amount of gypsum is that under the most ideal conditions for the storage of manure, requiring exclusion of air, conditions are created favorable to certain anaërobic bacteria, which may reduce the sulfate to sulfid. This in turn readily reacts with carbonic acid to form calcium carbonate, with simultaneous liberation of hydrogen sulfid. In this way, therefore, some of the gypsum is destroyed and its efficiency as a fixer of ammonia is consequently lost.

41. Gypsum safe to use. — As a manure preservative, gypsum possesses the distinct advantage of being a safe substance to use under the cows, in contrast to most or all of the other materials; for many of them are likely to injure the feet of the cattle unless their use is restricted solely to the gutters, or preferably to the manure as it leaves the stable.

42. Gypsum compared with other chemical preservatives. — It was found by Müntz and Girard, in the course of their experiments, that not only gypsum, but sulfate of iron, kainit, superphosphate, and calcium carbonate, had but slight efficiency as preservatives of dung, a result supported by the work of Julie and others. More recently, however, Severin, in laboratory experiments with unsterilized manure, as well as with sterilized manure subsequently inoculated with either watery extracts of manure or with pure cultures of organisms capable of causing ammoniacal fermentation, found that the addition of 4 per cent of gypsum to the manure increased the decomposition 10 to 20 per cent. It did, however, at the same time effect the preservation of the ammoniacal nitrogen which had been produced.

The efficiency of superphosphate as a preservative of manure depends primarily upon the gypsum associated with it. Its effect may be heightened in some cases by

the presence of small quantities of sulfuric acid which may have been used in excess, or by the presence of small amounts of free phosphoric acid. The solubility of the phosphoric acid of the acid phosphate is, however, greatly lessened when added to the manure, supposedly due to the appropriation of the phosphorus by the microörganisms present in the mass.

Further substances which have been employed at various times as preservatives of manure are kieserite (crude sulfate of magnesia), kainit, sulfuric acid, and moss impregnated with dilute sulfuric acid. Sulfuric acid has also been used for the preservation of liquid manure in the cisterns or receptacles in which it is sometimes collected and stored prior to its application to the land The sulfates, and even sulfuric acid, are all subject to the same reduction and transformation through the agency of anaërobic bacteria as gypsum, on which account they have sometimes proved disappointing as preservatives.

43. Preservation by antiseptics. — In order to stay or prevent fermentation in manures, the use of antiseptic substances has been proposed. Among these are carbon disulfid and soluble fluorids, but they are too expensive to justify the attempted saving in the manure. (See in a later chapter a discussion of the effect of carbon disulfid on soils.) An important consideration in this connection is that manures, to be sufficiently effective for the growing of early garden crops and for many other purposes, must have undergone a certain amount of fermentation of the proper kind and under proper control, before they are applied to the soil. It must be obvious, therefore, that the treatment of the manures with antiseptic substances may in the end interfere with the fulfillment of their most important function.

CHAPTER IV

THE ORGANISMS AND FERMENTATION OF DUNG

It is but recently that the enormous numbers of microörganisms, and hence the great significances of varying conditions upon the changes in animal excrement, have been fully recognized.

44. The number of microörganisms present in cow and horse manures. — When the solid excrement is voided, it is already swarming with microörganisms. In one gram (about one twenty-ninth of an ounce) of cow dung, which had been voided but one day, Wütrich and von Freudenreich found from 7,000,000 to 375,000,000 of organisms. The number reported more recently by other investigators has ranged from 7,000,000 to 90,000,000. In the dung of cows kept in the stall, Guper [1] found from 1,000,000 to 120,000,000 of organisms per gram, in contrast to but from 1,000,000 to 4,000,000 when they were at pasture.

Better perfected methods show still greater numbers. — It has also been claimed that the methods of the investigators just mentioned were such as to give figures below, rather than above, the truth, for by the later and better perfected methods, W. Hüttemann found in 0.1 c.c. of the intestinal content of cattle 1,000,000,000,000 microörganisms. In comparisons of the feces of cattle and horses, Stoklasa [2] found in a gram of the former 60,000,000 to

[1] Centralb. f. Bakt., II Abt., 22 (1909), 415.

[2] Fühling's Landw. Ztg., 56 (1907), 411.

90,000,000 of microörganisms, and in the same quantity of the latter, from 100,000,000 to 150,000,000.

Microörganisms in human feces. — In human feces, Matzuschita[1] found as high as 18,000,000,000 per gram. According to Nothnagel, the microörganisms in the feces of man often constitute the chief mass of the material, and J. Strasburger found that human feces contained from 17 to 68 per cent of these organisms. On the dung of sheep, List observed lumps consisting of many thousands of them. Still other investigators substantiate these high percentages.

45. Significance of microörganisms in manure. — It is evident from what has preceded that animal excrement can no longer be looked upon as a mere storehouse of plant food, but as a mass teeming with the most abundant life, and capable of undergoing quite different forms of decomposition and of yielding widely different products, according to the moisture, temperature, reaction, and the kinds and amounts of undigested and metabolic residues remaining therein.

46. Microörganisms in litter. — The number of microorganisms in straw litter has been found to range from 10,000,000 to 400,000,000 per gram. In peat, used for litter, Backhaus and Cronheim have reported from 2,000,000 to 3,250,000 of microörganisms per gram.

47. Urine, when voided, essentially free from microörganisms. — The urine of healthy animals, when it is voided, is either sterile or essentially germ-free. Its infection, however, results immediately upon being voided, and, being a good medium for promoting bacterial growth, it is soon teeming with millions of living forms. The addition of the liquid to the solid excrement results in a

[1] Archiv f. Hyg., 41 (1901), 210–255.

rapid increase in the organisms, which give rise to the formation of ammonia.

48. The numbers of bacteria decrease gradually. — Mixtures consisting of litter and of solid and liquid excrement are exceedingly rich in living organisms, although their numbers finally show a decrease. In manure fourteen years old, which had remained without chemical treatment and which had shrunk greatly in volume, there were found 12,500,000 microörganisms per gram; whereas in identical material, which had been treated with kainit and the gypsum residue from the manufacture of double superphosphate ("superphosphatgyps"), but 3,750,000 organisms were found per gram of manure.

49. The disadvantage of antiseptics. — The employment of distinctly antiseptic materials as additions to dung would still further lessen the number of microörganisms, or destroy some of them completely; and this fact, as mentioned in Section 43, has often been advanced as an argument against their use as preservatives of stable manure, since the value of the dung for certain purposes is enhanced by properly regulated bacterial activity of the right sort. To what extent and for how long this would hold true for the various antiseptic substances, provided the dung were reinoculated with suitable organisms, remains to be determined.

50. Types of microörganisms present in manure. — The micrococci and streptococci are generally less numerous in stable manure than the rod-shaped forms (true bacteria). In moist, well-composted manure, in which the conditions for anaërobic fermentation are good, the intestinal streptococci are marked biochemical factors. The importance of the micrococci under such conditions

is certainly small, and Severin [1] observed that the micrococci in horse manure which was kept under anaërobic conditions were soon destroyed.

In fresh cow dung Backhaus and Cronheim [2] found the relation of liquefying to non-liquefying forms of bacteria as 1 to 5.5; but after maintaining the material for two days at 18° C., the proportion was found to be as 1 to 3.5. In the fresh dung of other animals, however, the non-spore-forming, short-rod forms, belonging normally and chiefly to the coli-aërogenes group, were prominent. The fluorescens and proteus forms are both frequent among the liquefying groups. The brown to black fluorescens and putidum types are characteristic of manure. These are not only of importance in connection with the formation of ammonia, but they are also active, together with other closely related forms, in effecting denitrification.

51. Aërobic forms. — Aërobic, spore-forming bacteria of the mycoides, subtilis, and mesentericus groups are present in great numbers in both litter and solid excrement. These are also of importance in the formation of ammonia. Included in the foregoing groups are also some of the most powerful decomposers of urea, as well as the organisms responsible for the development of high temperatures in loose, open manure. Among the latter may be mentioned *B. subtilis*, which continues active in horse manure until it reaches a temperature of 71° C. In stable manure at 60° to 70° C., Dupont [3] found *B. mesentericus ruber*, but chiefly *B. thermophilus grignoni*. Neither attacked cellulose, but both decomposed the proteins energetically. The former attacked starch, sugar, and wood gum, whereas

[1] Centralb. f. Bakt., II Abt., 1 (1895), 804.

[2] Ber. landw. Inst. Königsberg, *2* (1898), 23, cited from Löhnis.

[3] Ann. Agron., *27*, 1902.

the latter attacked sugar but slightly and starch and wood gum not at all.

52. Spore-forming anaërobic forms. — The spore-forming anaërobic bacteria may be considered as regular inhabitants of the manure pile, although their presence, or at least their number, is dependent to a considerable extent upon the character of the food consumed by the animal producing the manure. Other forms, though frequently found in the liquid leachings of manure, are not of special agricultural importance.

53. Actinomycetes. — The actinomycetes are also found in stable manure, certain of which are capable of enduring high temperatures, and others, such as the "Strahlenpilze" are of importance in connection with the formation and decomposition of humous substances.

54. The yeasts. — Among the yeasts the monilia species and Torulaceæ and even the true saccharomycetes are present.

55. The molds and other organisms. — The molds often develop in manure to a serious extent, and at least *Oidium lactis* passes readily through the digestive tract uninjured, in which respect it differs widely from the yeasts. The molds are powerful destroyers of both nitrogenous and non-nitrogenous constituents of manure. This is especially true of very dry horse and sheep manure. In the former their growth is the chief cause of the phenomenon known as "fire-fanging."

Other organisms which occasionally develop upon fermented manures, in storage, but which are of relatively less agricultural importance, are the myxomycetes.

56. Animal organisms destroy bacteria. — The protozoa may possibly play an equally or even more important part in manure than the molds and yeasts, although their

action is but just beginning to be understood. The recent work of Russell and Hutchinson at the Rothamsted experiment station appears to show that in the soil at least amebe and perhaps certain other protozoa feed on living bacteria, in some cases to such a serious extent as to greatly affect the fertility of the soil. On this account such soils may be improved by heating and by the application of carbon disulfid, toluene, tricresol, chlorid of lime, and other substances which destroy the protozoa and give the bacteria a chance to gain the ascendency.[1]

The idea of the activity of microörganisms in the decomposition of stable manure is not new, for special attention was called to it by Kette in 1865.[2]

57. The effect of heating and of antiseptics on manure. — It was shown by Dehérain that the addition of chloroform to stable manure very largely, but not completely, prevented the formation of carbon dioxid, and that heating to a temperature of 85° C. caused the formation of methane to cease.

The elder and younger Schloesing found that stable manure heated at temperatures of from 70° to 80° C. continued to yield small quantities of hydrogen and carbon dioxid; but less than were produced after heating to temperatures below 70° C.

It has been shown by Severin,[3] that in completely sterilized manures the formation of ammonia ceased entirely, though losses of ammonia by volatilization and as a result of the reaction of sulfurous acid on amids, were nevertheless possible, due to chemico-physical phenomena.

[1] Science, *32* (1910), 370.

[2] Die Fermentationstheorie, etc., 2d ed., p. 58 *et seq.*

[3] Centralb. f. Bakt., II Abt., 1 (1895), 165 and 809.

58. Destructive changes in the non-nitrogenous matter of dung. — In the processes of decomposition taking place in animal manures, fats and carbohydrates are destroyed in large quantities. The loss of these substances is rarely, if ever, less than 10 per cent, and is often in excess of 50 per cent.

According to Stoklasa,[1] the dry matter of stable manure may contain 30 to 40 per cent of cellulose and 20 to 30 per cent of pentosans. In the dry matter of sheep manure and straw litter the amount of pentosans has been found by Dühring to be 20 and 29 per cent, respectively, and the corresponding percentages of cellulose were found to be 21 and 38. It seems probable that there may be wide variations in these percentages according to the character of the food consumed, for in the air-dry dung of sheep Weiser and Zaitschek report 3.6 per cent of pentosans and 3.2 per cent of starch; in the dung of swine they found under the same conditions 3.7 per cent of pentosans and 3.2 per cent of starch; and in the air-dry dung of oxen, 2.6 per cent of pentosans and 10.5 per cent of starch.

59. Losses not confined to the cellulose. — Certain earlier investigators were inclined to the belief that the chief loss of carbohydrates during the decomposition of animal manures was confined to the cellulose; yet more recent investigations by Miller show that 21.7 per cent of the original sugar was lost, also 18.6 per cent of the original pentosans, and but 8.7 per cent of the original cellulose. It was observed by Sjollema and De Ruyter de Wild, at a temperature of 35° C., that under anaërobic conditions the pentosans suffered heavy losses; however, they remark that this fact enhances greatly the final value of the manure.

[1] Fühling's Landw. Ztg., *56* (1907), 41.

According to Schloesing, organic matter loses more carbon than oxygen, but the hydrogen content remains unchanged when organic matter decomposes under exclusion of air.

60. Most of the aërobic and anaërobic organisms in dung are active. — The majority of the aërobic and anaërobic organisms present in horse and cow manures, have to do with the decomposition of the carbohydrates. Prominent among these are the aërobacter and amylobacter groups which give rise to volatile and non-volatile fatty acids, and to extensive gas production, the latter of which represents material losses of vegetable matter. *B. punctatum* has also been found to be a strong gas producer, and *B. fluorescens* is a powerful liquefier of starch.

61. Diastatic action. — Stable manure contains many organisms which exert a diastatic action, among which are the molds and the actinomycetes. Certain of the bacteria belonging to the mycoides, subtilis, and mesentericus groups act similarly at certain stages, but the yeasts have no diastatic effect whatsoever.

62. The decomposition of starch. — Starch is transformed by *B. mesentericus ruber* into carbon dioxid, formic acid, and valerianic acid; also sugar into carbon dioxid, acetic acid, and butyric acid. *B. suaveolens*, one of the proteus group, transforms starch into sugar, dextrin, alcohol, aldehyd, formic acid, acetic acid, and butyric acid. The action of the butyric acid bacteria upon starch has been found to result in the production of small quantities of ethyl alcohol, 35 per cent of butyric acid, and 9 per cent of acetic acid. This action, however, depends upon varying conditions, and certain members of this group may even fail to attack starch at all.

63. The decomposition of pectin. — Among the organisms effecting the destruction of the pectin of straw and manure may be mentioned the aërobic form *B. mesentericus ruber*. The organisms chiefly responsible for the destruction of pectin are, nevertheless, aided by high temperatures and the exclusion of air.

64. The decomposition of cellulose. — Cellulose appears to be capable of destruction by anaërobi organisms, denitrifying bacteria, and also by certain aërobic bacteria and molds. In manure, however, owing to the lack of oxygen and nitrates in the interior of the piles, the anaërobic bacteria become the chief factors in breaking up the cellulose.

It has been shown by the work of Omelianski and of Van Senus that certain organisms which are active in the formation of butyric acid (the group of *B. amylobacter*, Van Tiegham), which were supposed to destroy cellulose, do not attack it, or at least only when it is present in amounts not in excess of one per cent. In the latter case several of the fatty acids were formed, together with traces of higher alcohols and other substances, but the gases consisted of CO_2 and H, while CH_4 was entirely lacking. This hydrogen fermentation, produced by *B. fermentationis cellulosæ* is therefore different from the methane fermentation produced by *B. methanigenes* (Omelianski), Lehm and Neum, yet both acetic acid and *n*-butyric acid are produced by the latter. Whether the methane fermentation or the hydrogen fermentation shall dominate, seems to depend upon the existent conditions, but usually the methane fermentation is the first to develop. Both sets of organisms are, however, present in the intestinal tract of domestic animals and are therefore found in the dung when it is voided. It appears probable from experiments with other materials that the methane fer-

mentation may take place more readily in a neutral than in an alkaline medium. In this respect the conditions are quite the contrary of those favorable to the hydrogen fermentation. It is probable also that in open, strongly heated manure certain thermophilic decomposers of cellulose may be present. Furthermore, the particular kind and source of the cellulose may likewise be, to a certain extent, a factor in determining the nature of the resulting fermentations.

65. The decomposition of fats and waxes. — In so far as concerns the fats and the waxes, it appears probable that at least some of them may, under certain circumstances, undergo at least a partial breaking up by anaërobic organisms. Their destruction, which takes place readily in the presence of oxygen, is quickly affected by exclusion of air. The glycerine which is produced as a result of the process is itself quickly destroyed. This destruction may be caused by *B. boocopricus*, an organism present in cow dung, and give rise to methyl alcohol, and butyric, acetic, and formic acids.[1] In any event, the decomposition of the fats and waxes in the manure, when it is properly stored, takes place too slowly to have any great practical significance.

66. The decomposition of urea. — One of the first changes taking place in stable manure is the breaking up of the urea into ammonium carbonate and this finally into ammonia, carbon dioxid, and water, as indicated below: —

$$\underset{\text{urea}}{CO(NH_2)_2} = \underset{\text{water}}{2\,H_2O} + \underset{\text{ammonium carbonate}}{(NH_4)_2CO_3}$$

$$\underset{\substack{\text{ammonium}\\\text{carbonate}}}{(NH_4)_2CO_3} = \underset{\text{ammonia}}{2\,NH_3} + \underset{\substack{\text{carbon}\\\text{dioxid}}}{CO_2} + \underset{\text{water}}{H_2O}$$

[1] O. Emmerling, Ber. d. d. chem. Gesell., *29* (1896), 2726.

This transformation of urea into ammonia is usually practically completed in manure piles in from four to five days.

The discoverers of urea, Fourcroy and Vauquelin,[1] attributed the formation of ammonia to the fermentative action of certain slimy substances. That bacteria play a prominent part in this change was shown by the investigations of Alexander Müller [2] and Pasteur.[3] Many later investigators have studied the subject, until now the number of organisms known to effect the change of urea into ammonia is not only very great but also quite varied in character, embracing molds and particularly members of the various subdivisions of the Coccaceæ and Bacteriaceæ. Among the latter are embraced the non-spore-producing forms such as proteus, coli, and fluorescens, and certain of the red and yellow bacteria. Among the most powerful transformers of urea are some of the spore-producing bacteria, one of which, *Urobacillus pasteuri* Miquel, is capable of transforming three grams of urea per liter in a single hour. Included in the list of the more common forms found in stable manure are micrococci, *B. pasteuri freudenreichii;* also members of the fluorescens, proteus, and coli groups. Of these *B. pasteuri* requires nitrogen from other sources than urea, though many of them are fully able to depend upon urea for their nitrogen and as a source of energy, provided there are also at disposal small quantities of carbohydrates or salts of organic acids. In the case of *B. erythrogenes*, Söhngen found that, for every 20 milligrams of carbon supplied in suitable form, 500 milli-

[1] Annal. de Chemie, *31* (1799), 65.

[2] Jour. f. prakt. Chem., *81* (1860), 469 *et seq.;* (1863), 217 *et seq.*

[3] Comptes rend. (Paris), *50* (1860), 849–854; Ann. de chemie et de phys., (3), *64* (1862), 50–57.

grams of urea were transformed into ammonia; and in the case of *Urobacillus jakschii,* Söhng., the relation was that of 10 of carbon to 1800 of urea transformed.

There seems to be a wide diversity of opinion as to the rôle of enzymes in the transformation of urea.

The mass of bacteria required to transform a given quantity of urea is surprisingly small, since Miquel has shown that one part by weight of a culture of *Urobacillus duclauxii* was capable of changing 4000 parts of urea into ammonia, and Burchard, in experiments with *Microc. ureæ liquefaciens,* found it capable of transforming urea into ammonia to the extent of from 180 to 1200 times its own weight. Not only is the change rapid, and also great, in proportion to the mass of organisms acting, but it is likewise often practically absolute.

67. The decomposition of hippuric acid. — As compared with urea, hippuric acid is decomposed with much difficulty, the resulting products being glycocoll and benzoic acid, according to the following chemical equation: —

$$\underset{\text{hippuric acid}}{C_6H_5CO\cdot NH\cdot CH_2COOH} + \underset{\text{water}}{H_2O} = \underset{\text{glycocoll}}{CH_2(NH_2)COOH} + \underset{\text{benzoic acid}}{C_6H_5\cdot COOH}$$

The same organisms which actively promote this transformation also promote the formation of ammonia from the glycocoll.

Many of the organisms which produce ammonia from urea have the same action upon hippuric acid. Nevertheless, certain organisms which decompose the one do not appear to act strongly on the other. There are, in fact, certain specific decomposers of urea, hippuric acid, and of uric acid.

68. Changes produced in uric acid. — Under the influence of *B. arce* and of *B. fluorescens liquefaciens*, both urea and ammonia are produced.[1]

It was found by Giglioli that in a case of spontaneous infection of a solution of uric acid, only urea and carbon dioxid were formed, though Schellmann encountered under similar circumstances organisms capable of decomposing both uric acid and urea.

By the action of *Penicillium glaucum* uric acid is transformed into ammonia, although *Aspergillus amidase* has no effect upon it. Without attempting to go into the details of the subject, it suffices to state that uric acid very readily yields ammonia under the conditions of fermentation usually existent in dung heaps.

69. Ammonification of solid manure and litter. — Under the conditions accompanying the usual normal fermentation of stable manure, the quantity of ammonia actually produced from the nitrogenous substances of the solid excrement and of the litter is very small. It has been shown repeatedly that a condition most favorable to the formation of ammonia from such substances is exclusion of air. In an experiment by Jentys[2] only one per cent of the nitrogen of solid excrement was changed into ammonia in the course of one month under free access of air, but, in an artificial atmosphere of nitrogen, 11 per cent of nitrogen was changed into ammonia in the same period of time. In experiments with a mixture of manure and straw, Dietzell[3] found that but 3 per cent of the nitrogen was changed into ammonia at the end of six

[1] F. and L. Sestini, Landw. Vers-Sta., *38* (1890), 157–164.

[2] Anzeiger d. Akad. d Wissench., Krakau (1892), 194; cited from Löhnis.

[3] Landw. Vers-Sta., *48* (1897), 163 *et seq.*

months, in case care was taken to secure good aëration; but that under exclusion of air about 20 per cent of the nitrogen had been changed into ammonia. The conditions therefore best suited to the formation of ammonia from urea are, according to the authorities just mentioned, quite the opposite of those essential to the production of ammonia from the solid excrement. On this point, however, Dehérain and Dupont [1] disagree with the other investigators, for they hold that under anaërobic conditions the transformation of the albuminoid substances of the solid excrement and of the litter into ammonia is very slight, and that it takes place far more readily in the presence of air.

The reasons for the slowness of the formation of ammonia in the solid excrement are made perhaps more appreciable when one recalls that it is composed, to the extent of one-half of its nitrogen content, of the materials which have already resisted the action of the digestive ferments of the stomach or stomachs and of the intestines; and that approximately the other half of the nitrogen is in the bacteria and other lower organisms voided with the manure. The importance of this point is further emphasized by the fact that the organisms mentioned are rich in nuclein compounds, and in chitin, all of which are highly resistant to decomposition. Furthermore, the antienzymes present in the living organisms afford a certain resistance to their decomposition and destruction, even for a considerable time after their life-functions have ceased.

70. Terms used in discussing the decomposition of dung. — Most of the earlier writers have attempted to

[1] Ann. Agron., *27* (1901), 401–427; Abs., Zentralb. f. Agr. Chem., *31*, 240.

classify the different stages or conditions of the decomposition of animal manures, as fermentation, eremacausis, molding, or putrefaction, but no definite lines of demarcation of these processes, resting upon a scientific basis, has been found possible. It is, however, quite customary to consider the last two processes as taking place under exclusion of air, and by many the last is held to relate chiefly to the changes in animal matter, though certain writers apply it equally to the changes in the vegetable proteins. For the promotion of eremacausis, on the contrary, free access of air is an absolute necessity. The production of ammonia was considered by W. Eber [1] as a sure indication of putrefaction, whereas others have considered that the formation of skatol, indol, ammonia, hydrogen sulfid, or aromatic substances gave such indications. Some writers, in agreement with Pasteur,[2] consider the term applicable only to the decomposition of the protein bodies under anaërobic conditions and as inapplicable to their decomposition when caused by certain aërobic organisms (proteus forms). It has been proposed by Hiller [3] that, in place of the previous indefinite terms, there should be substituted hydration, reduction, and oxidation. It has been pointed out also that it depends upon the existing conditions whether the changes that take place in a given lot of manure shall receive the one or the other designation. As these changes cannot be based on definite chemical or biochemical processes, owing to the variations in the character of the materials at different times and in different parts of a pile of manure, there seems to be little gained in attempting

[1] Zeits. f. Fleisch und Milchhyg., *1* (1891), 118.
[2] Comptes rend. (Paris), *56* (1863), 1189–1194.
[3] Die lehre von der Fäulniss (1879), 18–33 and 47.

to give to these terms more than their original very general significance. One should, therefore, by all means avoid their use wherever definite scientific terms can be employed.

71. The nature and cause of the losses occurring in manure. — It should be borne in mind that the change of urea into ammonia is the result of two stages of transformation; first, to ammonium carbonate, and then to ammonia and carbon dioxid. If the reaction could be stopped at the end of the first stage by maintaining plenty of moisture and an excess of carbon dioxid, and if the exclusion of the air could also be accomplished, the second stage would not readily follow. Under the usual conditions, however, not only in urine itself, but also in the usual dung heap, the free movement of the air causes the removal of the excess of carbon dioxid, thus creating conditions favorable to the dissociation of a part of the ammonium carbonate. In addition to the direct volatilization of ammonia due to the previous loss of carbon dioxid, ammonia is also subject to direct oxidation into nitrogen gas and water. This change is readily effected by bacterial action when the manure pile is open and loose, so that the air gains free access. Even though the production of carbon dioxid takes place abundantly under such conditions, it is naturally dissipated into the air, thus rendering little aid in preventing the dissociation of the ammonium carbonate and the consequent loss of ammonia.

72. Losses less by fermentation when moist and compact. — In cases where the manure is kept very moist and well trampled from the outset, the aërobic processes just described are replaced, after the consumption of the small volume of oxygen in the mass, by those of an anaërobic character, giving rise to abundant hydrogen and carbon

dioxid, under conditions which preclude the ready escape of ammonia. Following the period of the more rapid evolution of hydrogen (which is determined by the continued presence of oxygen and the time required to effect the destruction of the more readily decomposable carbohydrates), the evolution of methane increases greatly, accompanied also by evolution of carbon dioxid, the formation of water, and the destruction of much of the cellulose. The rise of the temperature of the pile, due to the changes induced by the utilization of the oxygen by the aërobic bacteria present in the mass, is soon followed by a material drop in the temperature.

73. Losses increased by bacteria from intestinal tract. — Aside from the changes which have been mentioned, still others initiated by bacteria from the intestinal tract (among which is *B. coli communis*), aided by microorganisms present in the air, bring about the destruction of the proteins and effect their transformation into amids, amino-acids, and eventually ammonia. These changes are accompanied by the formation of various fatty acids, chief among which is butyric acid.

74. Losses smaller in the later stages of decomposition. — It is a notable fact that in the later stages of the fermentation of stable manure, only small direct losses of ammonia take place. This is readily understood, in view of the enormous numbers of bacteria and other organisms involved in the many transformations taking place in the nitrogenous and non-nitrogenous portions of the litter and manure; for considerable quantities of the ammonia are built up into the structure of the organisms themselves, whereby it becomes less subject to material loss, though depreciating greatly its immediate manurial efficiency. In other words, the ammonia becomes transformed, by

this process, into combinations similar to those existing in the soil humus.

As a result not only of the fermentation of the carbohydrates, but also of the proteins of the dung and litter, organic acids are formed, which are neutralized by the ammonia. Carbonates of the alkalies are likewise produced in the course of the destructive processes, and these, by their solvent action upon the dead bacteria, give rise to the dark liquors which are characteristic of the leachings of old dung heaps.

Least when only the ammoniacal stage has been reached. — The best results are to be expected from manure which has passed only to the second or ammoniacal stage, rather than from that which has reached the most advanced stage of decomposition, for the ammonia is then ready to undergo immediate nitrification as soon as the manure is brought into the soil. Furthermore, at this stage the vegetable matter is so far destroyed as not to have a serious effect upon plants or to greatly promote the destruction of nitrates in the soil. At the same time, also, there is much material still present in forms suitable for promoting the growth of such organisms as assimilate nitrogen directly from the air, which, in their turn, add to the store of nitrogen in the soil.

75. Fresh manure lacks immediate effectiveness. — The idea has been handed down from early in the last century that fresh stable manure can be employed with the best results only when considerable time elapses between its application and the date of planting. The effect of fresh manure is said to be worse in light soils than in those which are heavy. Many writers insist that the straw in the litter should be quite well broken up by the processes of decomposition before its application. The time nec-

essary for the accomplishment of this varies greatly with the location and the season. It would naturally take place more quickly in a moist, warm climate than in one which is dry and cold. In the winter these desired changes may require a period ranging from eight to twenty weeks.

76. The great necessity of moisture in heaps of solid manure. — From what has preceded, it appears that the best condition for the preservation of solid manure is that it should be kept moist by the liquid excrement, or, if this is insufficient, by additions of water. This is well recognized in France and other European countries where the manure is kept under cover, and is so situated that any seepage from it may be pumped back again upon the top of the pile. If in such cases a considerable loss of liquid results by evaporation, water is added to replace it. For a similar reason it is a more or less common practice among gardeners who buy large quantities of stable manure, to be stored in piles in the field, to have the tops of the piles incline towards the center so that they will catch rather than shed the rainfall. This prevents too rapid changes and the losses due to the presence of oxygen and the consequent rapid multiplication of undesirable classes of microörganisms.

77. The preservation of the liquid manure. — It is important in the preservation of the liquid manure that it be subjected to both the chemical and physical absorbent action of the litter. If the liquid manure is collected in a cistern or reservoir by itself, the receptacle should be closed tightly in order to prevent the passage of air currents over it, for the ideal condition for the preservation of liquid manure is to have it covered with a layer of carbon dioxid gas which prevents the rapid dissociation of the ammonium carbonate. It is probably safe to assert that

even if the greatest care is taken to preserve the liquid manure as completely as possible by itself, there is nevertheless more loss than if it is mixed with the solid manure and is then spread on the soil at once or at frequent intervals.

CHAPTER V

THE PRACTICAL UTILIZATION OF MANURES

THE important feature in connection with manures is that what has been learned in relation to their fermentation and conservation be applied in a practical way, and these matters will now be discussed in detail.

78. Storage *versus* direct application of manure. — It is still a much discussed subject whether stable manure should be allowed to lie in the stable or under a shed until needed, or whether it should be hauled to the field and spread as rapidly as it is produced. At all events, if the choice lies between its remaining for several days or weeks in a loose heap before it can be spread, especially in the summer time, or its being trampled down and preserved at once, together with the liquid manure, no doubt the latter is by far the better method of storage. If, however, the manure can be hauled out daily and incorporated with the soil at once, the greatest possible conservation of the nitrogen will result. If the manure is spread broadcast in the field just prior to a rain, the soluble portion will be carried into the soil, and the loss of nitrogen will then be reduced nearly to a minimum.

The danger of the loss of manure on ordinary slopes, under usual conditions, by surface leaching, is not great unless the soil is exceptionally impervious and the rainfall unusually heavy and long continued. Applications should, however, never be made on such locations when the land is frozen deeply or when it is covered with a thick bed of ice.

When the ground is fairly level and is not frozen materially, even if covered with light or moderate amounts of snow, the dung of horses and cattle can be applied with much safety.

There is much to be said from a practical business standpoint in favor of the direct application of such manures to the land, even aside from the prevention of manurial losses. If they are not applied as produced, the farmer finds himself seriously handicapped in the spring by the necessity of hauling them out when the planting should be in progress, and thus a series of delays and consequent losses often follow throughout the year.

79. Immediate incorporation of manure with the soil. — From the standpoint of the conservation of the ammonia, probably no more rational advice could be given than that by Dehérain, to the effect that a shallow furrow should be turned over the manure, if possible, as rapidly as it is applied to the land. In view, however, of the great cost of labor in the United States, a second plowing of the land, such as would be required by this method, would hardly make it an economical proposition. On light soils, it would be more advisable to turn the manure under in one operation, to the usual depth of plowing, and on heavy soils to spread it after plowing and then incorporate it with the soil by immediate harrowing.

80. Losses occurring in heaps in the field and if broadcasted. — If well fermented manure must be hauled to the field a considerable time before it can be incorporated with the soil, either by plowing or harrowing, the ammonia will be best conserved if it is placed in large piles. In case it is left in small heaps, as was formerly the common practice in New England, until it is convenient to spread it, the sun dries out the liquid, the winds carry away the car-

bon dioxid, the dissociation of the ammonium carbonate is thus facilitated, and the ammonia is rapidly volatilized. One of the most serious wastes which can occur is from leaving such manure spread for a long time upon the surface of the ground in pleasant weather, exposed to the sun and wind. Under such conditions, great losses of ammonia are inevitable. As compared with the losses which may result in this manner, those due to the usual application of fresh manure directly to the soil are probably very small.

81. The time to spread manure on fields. — If on any account partially fermented manure must be allowed to lie on the surface of fields for some time before it can be incorporated with the soil, its application should preferably take place just prior to or during a fall of rain, or upon a light, fresh fall of snow, in order that the ammonium carbonate may be carried directly into the soil, for, as explained previously, the soil readily absorbs and holds ammonia, excepting under conditions not commonly met with in agricultural practice.

82. Certain vegetable substances aid denitrification in manures. — The scientific study of the management of animal manures was taken up a few years ago with renewed interest as a result of inducements offered by the Deutsche Landwirtschafts Gesellschaft (German Agricultural Society). In the course of this work it was found by several German investigators that the solid excrement of certain farm animals was worse than useless, for, by its incorporation with the soil, crops were lessened rather than increased. This led to a study of the action of straw in order to learn if it, or solely the solid excrement with which it was commonly associated, was responsible for this effect. As a result, it was found that straw also, when incorporated with the soil, often lessened rather than in-

creased the yields. The further pursuit of the problem led to the discovery that the ill effects resulting from the employment of the straw and the fresh excrement of farm animals, in large quantities, were caused chiefly by the destruction of the nitrates within the soil, whereby a large portion of their nitrogen was liberated from the soil as free nitrogen gas, and in consequence the plants suffered from nitrogen hunger. It was also believed for a time that this ill effect of straw was because of its being a possible carrier of the denitrifying organisms and that its malign influence was directly attributable thereto.

83. Losses by denitrification less serious if used moderately. — As a protest against the foregoing results and against the conclusions drawn therefrom, attention should be called to the common experience of farmers and also to the long-continued experiments with animal manures at Rothamsted, England, from which their immediate, as well as their long-enduring, effects are evident. Furthermore, at Rothamsted the yields were greatly increased by supplementing the barn-yard manure with nitrates, from which it is evident that the latter were probably not wholly destroyed. In this connection much credit is due to Dehérain for pointing out the fact that in many of the German experiments, which were mostly conducted in pots, boxes, or small soil receptacles of various kinds, the ratio of the manure and straw to the soil was far greater than is customary in actual field practice, where, excepting in truck farming, only from four to ten cords of manure per acre are usually employed. It was also pointed out by Dehérain that with all of the other conditions uniform, starch and other carbohydrates, including the pentosans, became the determining factors in causing the destruction of nitrates. In fact, it was shown conclusively that by the

use of unduly large amounts of straw and of solid manure, the soil became well supplied with the carbohydrate foods required by the denitrifying organisms, whereby their multiplication in the soil and their activity as destroyers of nitrates were greatly increased.

From what has preceded it appears that the greatest economy in the use of coarse animal manures in the field is probably effected by the use of small or moderate applications, rather than by large ones. These observations also show another reason why partially rotted manure is much superior, for inducing quick growth, to comparatively fresh manure; for the former is much more heavily charged with food for the denitrifying organisms than that which has undergone a greater amount of fermentation.

84. Other factors affecting losses by denitrification. — It is obvious, also, that the manure of animals which have digested their food the most thoroughly is less likely to induce denitrification than that which is less completely acted upon by the digestive agents. The effect of manure in inducing denitrification is obviously determined, to some extent, by the character of the food consumed.

It has been shown experimentally that if a given amount of vegetable matter is introduced into the soil in a coarse condition and in a manner which does not admit of a complete admixture with the soil, it is less serious by way of inducing the destruction of nitrates than when the same material is ground and carefully mixed with the entire mass of the soil. The explanation is that in the latter case food is present at every point in the soil for the denitrifying organisms, which insures their general distribution and consequent greater destruction of nitrates than would be possible if they were only distributed here and there wherever the coarse portions of vegetable matter happened

to be present. Herein is found a partial explanation of the alleged better results secured on certain soils by plowing under the manure than by harrowing it into the soil in a thorough manner.

85. The lasting effect of stable manure. — Notwithstanding all that has been said about the immediate action of *large quantities* of litter and of solid manure by way of favoring denitrification, their beneficial after effects in the soil are of long duration, as the Rothamsted experiments have fully demonstrated. In this connection Director Hall of the Rothamsted station gives the results on grass where stable manure was applied at the rate of 14 tons per acre per annum for eight successive years (1856–1863), the land then being left in grass without manure or fertilizer for forty years. These results are compared with those secured on a similar field to which no manure was applied. The greatest increase over the unmanured area was in 1865, two years after the last application was made. The gain in that year amounted to 120 per cent. In the decade from 1866 to 1875, and for the three decades thereafter, the average increase in the produce, due to previous applications of manure, was 57, 24, 6, and 15 per cent, respectively.

In connection with the Rothamsted barley experiments, one plat received 14 tons per acre of stable manure for each of the twenty years from 1852 to 1871; a second plat has received the same amount per annum continuously; and a third has had none. The results show that the yields are still more than twice as great on the plat which received the manure for the twenty years as where none has been applied. The yields are now, nevertheless, only about 40 per cent of what they are where the application of manure has been continuous. Attention is called,

however, by Hall to the fact that such a long duration of the effect of residues of farm-yard manure would not be perceptible in ordinary farm practice, and that they only become apparent when the soils are cropped to a state of exhaustion which is most unusual.

86. Manure profitably supplemented by chemical fertilizers. — Where farm-yard manure commands a high price, or where the cost of hauling is great, it is usually better economy to employ only moderate amounts and to supplement it with chemicals, than to place entire dependence upon it. This is well shown by experiments at Rothamsted in which the use of 200 pounds of nitrogen in stable manure resulted in a yield of but 27.2 tons of mangel wurzels, as compared with a yield of 33 tons where but 86 pounds of nitrogen were applied in nitrate of soda, which was properly supplemented with potash and phosphoric acid. The farm-yard manure used with the same amount of nitrate of soda gave a yield of 41.4 tons, and when further supplemented by potash and phosphoric acid, the yield was only increased about 0.1 ton. Had the precaution not been taken to add potash salts with the manure and nitrate of soda, there would have been reason for concluding that the differences in yields were possibly attributable to the soda of the nitrate of soda, rather than to the nitrogen. This is evident from the experiments conducted at the Rhode Island station, in which it was found that the yield of mangel wurzels could be doubled by the employment of either sodium carbonate or sodium chlorid, even when as much as 330 pounds per acre of muriate of potash, or its equivalent of potassium carbonate, had already been used in the manures. In this case, however, it was found to have been probably due not alone to possible liberation of pot-

ash from the soil, but to direct substitution of the soda, for at least a part of the potash, in connection with the requirements for bases, or in one or more of the physiological functions of the plants.

87. Factors governing use of manure and chemicals. — If, in the operations of the farm, the products can be fed at a good profit, so that the farm-yard manure can be secured as a costless by-product in sufficient quantities to meet the entire manurial needs of the farm, it should be used as generally as possible even for the top-dressing of grass land. It may even be used in connection with the potato crop, under favorable conditions, provided the "seed" tubers are properly treated with formalin or corrosive sublimate solution for the prevention of scab.

If the supply of manure is small, the potato crop is one for which chemical fertilizers can usually be substituted to good advantage, particularly as the fertilizers are more likely to produce a crop free from scab and from insect injury.

88. The use of coarse manures. — If the manure is coarse, by virtue of being mixed with bulky litter, it is poorly adapted to the top-dressing of grass land. For such purposes the employment of fresh manure during the late autumn and in the winter months may be permissible, if there is no better use for it elsewhere. For spring top-dressing the manure should by all means be fine, and, if applied at such times as to avoid excessive losses of ammonia, it may be well rotted. The application of coarse manure may not only smother the grass, but there is also danger that some of the material will finally be raked up with the hay. On account of the fact that the soluble ingredients of manures diffuse but little laterally in the soil, it is important that top-dressings be very evenly

distributed, but this is difficult of accomplishment if the manure is excessively coarse.

If the manure is coarse and it is used on light soils, it may be plowed under, but if it is fine and it is to be applied to rather heavy soils, it is usually considered preferable to harrow it into the soil. As a general rule, farm-yard manure should be applied to hoed crops.

89. Reason for even spreading of manure. — The failure of fertilizers and manures to move laterally in the soil has been abundantly observed at Rothamsted, and it may be readily seen where a soluble chemical fertilizer is applied to grass land, for even after abundant rains the effect is often hardly visible for more than an inch or two beyond the limit to which it has been spread.

90. Manure favors the disintegration of old soil. — In breaking up old grass fields, the soil of which is in poor tilth, it is advisable to spread a small amount of stable manure broadcast before plowing, since it will serve as an efficient aid in hastening the decomposition of the turf, which is one of the first and most important steps in the line of effective soil improvement. This may be followed, if required, by an application of lime, which should be most thoroughly harrowed into the soil. Support for this proposed method of using stable manure is afforded by the recent experiments of A. Koch,[1] who inoculated mixtures of soil and cellulose, with ordinary soil, compost, barn-yard manure, and sewer slime. The average amount of cellulose consumed in six months amounted to 1.2 grams when soil was employed, to 3.85 grams with compost, to 10.35 grams with farm-yard manure, and to 1.85 grams with sewer slime. The average amount of nitrogen finally present in each, in milligrams per 100 grams of

[1] Abs. E.S.R. 27 (1910), 429.

dry soil, was 10.73 with soil, 92.05 with compost, 117.27 with stable manure, and 87.15 with sewer slime. From this it will be seen that the organisms present in the stable manure rendered possible the use of the cellulose as a source of energy in connection with the fixation of atmospheric nitrogen. Thus the introduction of stable manure into the soil, even in small quantities, may not only aid the decomposition of the excess of grass roots, whereby the general tilth is improved, but it may also aid materially by encouraging the growth of those organisms which assimilate atmospheric nitrogen, quite independent of the growth of legumes.

CHAPTER VI

SEA-WEEDS

Under the name of sea-weeds are sometimes grouped not only the marine algæ, but occasionally other marine plants, one of the most common of which, on certain coasts, is the eel-grass, or grass-wrack (*Zostera marina*), which belongs to the Naidacæ or Pond-weed family.

The number of marine plants which are not algæ is very small on the New England coast, and is said to hardly exceed half a dozen.

Fig. 2. — Sea-weed for Fertilizing.
Ribbon-weed, kelp, tangle (*Laminaria saccharina*).

91. The value of sea-weed known to the ancients. — The use of sea-weed as a manure was already well known to

the early Romans, as is shown by the writings of Palladius, who stated that after washing with fresh water, it, with other substances, can take the place of manure. Sea-weed has long been used for manurial purposes in the islands of Thanet and Jersey; also in the Hebrides, Scotland, England, Ireland, Wales, Sweden, and elsewhere.

PERCENTAGE COMPOSITION OF SEA-WEEDS [1]

	WATER	NITROGEN	PHOSPHORIC ACID	POTASH	LIME	MAGNESIA
Ribbon-weed, kelp, or tangle (*Laminaria saccharina*) [2]	88.0	0.17	0.05	0.16	0.38	0.17
Broad ribbon-weed, broad-leafed kelp, devil's apron, or tangle (*Laminaria digitata*) [2] . . .	87.5	0.23	0.06	0.31	0.41	0.22
Dulse, or dillisk (*Rhodymenia palmata*) [2] . . .	86.3	0.37	0.09	1.07	0.46	0.09
Round-stalked rock-weed (*Ascophyllum* (*Fucus*) *nodosum*) [2]	77.3	0.24	0.08	0.64	0.48	0.35
Flat-stalked rock-weed (*Fucus vesiculosus*) [2] . .	76.6	0.38	0.12	0.65	0.45	0.31
Phyllophora membranifolia [2]	66.2	1.08	0.14	0.96	5.11 [4]	0.69
Irish, or Carragcen, moss (*Chondrus crispus*) [2] . .	76.0	0.57	0.13	1.02	0.49	0.33
Cladostephus verticillatus [3] .	71.2	0.45	0.22	1.42	0.87	0.36
Polyides rotundus [3] . . .	58.5	0.70	0.16	1.45	0.37	0.46
Ahnfeldtia plicata [3] . . .	59.0	1.35	0.25	0.59	0.98	0.29
Eel-grass, or grass-wrack (*Zostera marina*) [2] . .	81.2	0.35	0.07	0.32	0.51	0.32

[1] A tabulation of analyses of sea-weeds by a number of analysts, in several different countries, all of which are reduced to a dry basis, may be found in Bulletin No. 21, Rhode Island agricultural experiment station, pp. 34–36.

[2] Average of samples taken in January, March, and September.

[3] Samples taken in September.

[4] More or less small shells adhered to the plants, which explains the exceptionally high lime content.

92. Chemical composition of sea-weeds. — Most of the earlier analyses of sea-weed were of the ash rather than of the entire plant. In many cases either the moisture content of the original plant was not given, or no distinction was made between "pure" and "crude" ash, on which account it is impossible to calculate the composition of the plants from which the ash was secured. On this account the number of analyses of sea-weeds in their natural condition is small, a fact that is regrettable for the reason that most of the sea-weeds used for manurial purposes, at least in the United States, are applied to the soil without drying, composting, or burning.

FIG. 3. — SEA-WEED FOR FERTILIZING. Broad ribbon-weed, broad-leafed kelp, devil's apron, tangle (*Laminaria digitata*).

The analyses on the opposite page by Wheeler and Hartwell show the composition of several different varieties, following the rinsing off of the salt water and the removal of the superficial moisture.

93. The composition varies at different seasons. — With but few exceptions, samples of sea-weed brought up

by the tide and collected on the shore in January and March were found to be richer in nitrogen, potash, and phosphoric acid than those collected in September. This may possibly be accounted for in part by previous partial drying in the warmer month of September, on account of

Fig. 4. — Sea-weed for Fertilizing.
Dulse, dillisk (*Rhodymenia palmata*).

which the specimens suffered some loss by leaching either in the sea-water or by falling rain.

94. Sea-weeds of chief importance in New England. — Among the sea-weeds which are most abundant on the New England coast, the Irish moss is one of the best. This is followed in value by the dulse (dillisk), the flat-stalked rock-weed, the round-stalked rock-weed, and finally by the kelps. The other varieties of the algæ

mentioned are found in such small quantities as to be of only minor agricultural importance.

95. The value of eel-grass. — The eel-grass, unlike the algæ, decomposes very slowly, and hence is not suitable for the top-dressing of meadows. For the same reason

FIG. 5. — SEA-WEED FOR FERTILIZING.
Round-stalked rock-weed (*Ascophyllum*, or *Fucus*, *nodosum*).

it is less valuable when turned under as a manure, and it may even act injuriously in such cases if used in large quantities in a dry season. The best method of using it is as litter for swine or other farm animals.

96. Value limited by distance of land. — The usual limit of distance to which sea-weed has been carted inland in the United States is from eight to ten miles, but even

then in some cases it is not profitable, if the teams and laborers can be employed economically for other purposes.

97. Practical utilization. — Such sea-weeds as decompose most readily can be used for the autumn and winter top-dressing of grass lands, provided they are not employed in such quantities as to smother the grass. As a rule, however, they can be used to the best advantage on land which is about to be plowed. Sea-weeds are generally considered preferable to stable manure in so far as concerns their effect upon the smoothness of the potato crop; but in regard to the cooking qualities of the tubers, unfavorable results from their use have been reported. It has in fact been shown by experiments at the agricultural experiment station in Rhode Island that the difference in the smoothness of the tubers is due to the alkaline effect of the farm-yard manure on the one hand, which creates conditions favorable to the development of potato scab, whereas common salt and other chlorids, such as are associated with sea-weed, have the opposite tendency. Furthermore, sea-weed itself would not exert an immediate alkaline effect, like farm-yard manures.

98. Effect on the quality of certain crops. — As concerns the effect of sea-weeds on the cooking quality and the composition of the potato, it must be borne in mind that if not leached they carry common salt, and that Schultz (of Lupitz), Salfeld, and other German experimenters have shown conclusively that the application of chlorids, just before planting the potato crop, results in a depression of the starch content of the tubers, increasing at the same time their nitrogen content, and causing the frequent development of a disagreeable soapy taste.

On account of the adhering sea-water, sea-weed may also

be injurious to hops, to the burning quality of tobacco, and it may depress the sugar content of beets. It is because of this well-recognized action that it has become customary, in certain countries, to allow the sea-weed to be leached by rains before carting it upon the land used for farming purposes. The same result is often accomplished in part on the coast of New England, without thought of

Fig. 6. — Sea-weed for Fertilizing.
Flat-stalked rock-weed (*Fucus vesiculosus*).

this feature, by the practice in times of storm of carting the sea-weed into piles a short distance from the shore, until a favorable opportunity is presented for hauling it away. This possible danger from the use of sea-weed may be very largely or wholly obviated by applying it either the autumn or winter previous to the time when crops subject to such injury are to be grown.

99. Sea-weed quick in its action. — Owing to its undergoing ready decomposition, sea-weed is to be classed

as a quickly acting manure, which exerts its chief effects the first season.

100. Sea-weed compared with farm-yard manure. — In the Western Islands, a load of farm-yard manure is considered as being equal to two and one-half loads of fresh sea-weed, or to one and three-fourths loads of sea-weed which has lain in a pile for two months.

101. Sea-weed not a well-balanced manure. — It is well recognized that sea-weed is not a well-balanced manure for all soils and crops, and that to supply the needed amounts of phosphoric acid in sea-weed, in all cases, would result in a frequent waste of potash or nitrogen, or of both. On this account, sea-weed should be supplemented, especially where the cost of hauling is great, by bone meal, basic slag meal, acid phosphate, or other phosphatic fertilizers.

102. Sea-weed as affecting the need of liming. — In case sea-weeds are used frequently and they carry, attached to them, a considerable quantity of the shells of mollusks, these will supply more or less carbonate of lime, and thus render liming unnecessary, whereas if they are very free from shells, they may ultimately have the opposite effect.

103. Freedom from weed seeds a great advantage. — A strong point in favor of sea-weeds, as compared with farm-yard manure, is their freedom from weed seeds. It is stated that on this account farmers in certain sections apply the farm-yard manure to their grass lands and reserve the sea-weed for their hoed crops. It is indeed related by M. Hervé Mangon [1] that on an island off the coast of France (Noirmoutiers) cattle are kept in large numbers, but the dung is dried and used as fuel; the ashes

[1] Comptes rend., *49* (Paris, 1859), 322.

of the dung and the native sea-weeds being the only manures used there for centuries.

104. Composting sea-weeds. — The composting of sea-weeds, as is frequently recommended in Europe, especially in Sweden and other cold countries, is not usually considered economical in the United States on account of the cost of labor involved in handling them. Sea-weeds

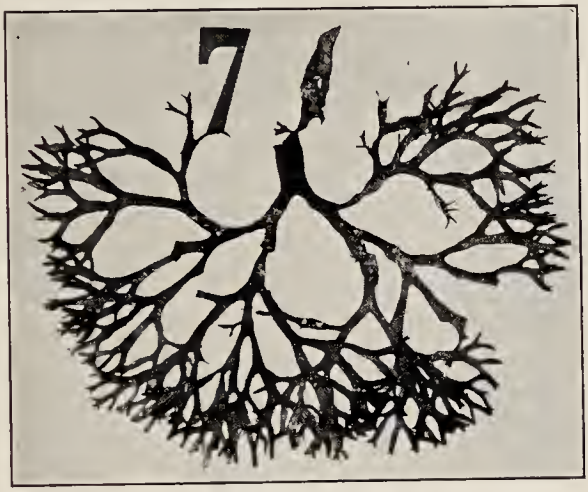


Fig. 7. — Sea-weed for Fertilizing.
Irish, or Carrageen, moss (*Chondrus crispus*).

are composted to a considerable extent on the coast of Brittany, France; and Turner tells of their being composted in Devonshire, England, where they are often piled in layers, each from 6 to 8 inches deep, with a quantity of lime scattered between. The pile is then turned over occasionally, and at the end of from two to three months, when well rotted, it is ready for use. Sea-weeds are also often composted with stable manure, but whatever the method followed it is a wise plan to keep the pile covered

with at least a thin layer of moist soil, in order to prevent the possible loss of ammonia.

105. Size and rapidity of growth of sea-weeds. — A good idea of the rapidity of the growth of sea-weed is furnished by an instance in Scotland where a rock, which was uncovered only during the lowest tides, was chiseled smooth in November and was thickly covered by the following May with sea-weeds ranging in length from 2 to 6 feet. The growth of certain of the giant sea-weeds of the Pacific coast and elsewhere must be exceedingly rapid, for some of these plants are said to be annuals propagated from spores; and specimens of *Nereocystis luetkeana* (Mertens) Postels and Ruprecht, for example, have been observed, that were over 300 feet long. Furthermore, McFarland (Fertilizer Resources of the United States, Senate Document No. 190, 62d Congress, 2d Session) also reports them 100 feet in length.

The giant kelp (*Macrocystis purifera*, Turner) (Agardh.) is said to be attached to the bottom by a holdfast which reaches three feet in diameter. The stem at first branches equally, but the later divisions grow to unequal lengths, some of which often extend to from 300 to 700 feet; and in exceptional instances the total length of some of these plants has been said to be fully 1500 feet.

CHAPTER VII

GUANOS

The name "guano" is derived from the Spanish word "Huano" which means dung. Its use for agricultural purposes dates, according to Garcilaso de la Vega, from the twelfth century, and in the year 1154 it is known to have been carried to Edrisi in Arabia. The European travelers Feuillé, in 1710; Frezier, in 1713; and Ullao, in 1740, all speak of the great value of guano as a manure.

106. Experimental trials of guano. — In 1804 Alexander von Humboldt took some guano to Germany, where it was examined chemically. At the instance of Sir John B. Lawes experiments were conducted with it by General Beatson at St. Helena in connection with the growth of potatoes, with most beneficial results. In 1824 Skinner of Baltimore received two casks of guano which served to demonstrate its value in the United States.

107. Commercial introduction into Europe. — The first attempts at the introduction of guano into Europe, in a commercial way, in 1835 resulted in failure; nevertheless in 1840 Quiros Allier & Co. of Lima made a shipment to Liverpool which was given a trial by the Royal Agricultural Society. The results were so good that the company made a six-year contract with the Peruvian government for the exclusive export of guano. The contract was signed on December 17, 1840, and in March of the following year the shipment was begun. It was continued

with such success that by October of that year twenty-three ship-loads had been sent to Europe. One of these vessels carried to Germany the first consignments made to that country. This was followed by a vessel load in February, 1842.

Reports of the high prices received for the guano in England soon caused the Peruvian government to withdraw its contract and to enter into more favorable four-year contracts with several firms.

108. The general nature of guano. — Guano is popularly supposed to consist exclusively of the excrement of sea-fowl which roost upon the islands or mainlands in great numbers, especially at night. Other common constituents are the feathers, bones, and bodies of the birds themselves, and the excrement and remains of large marine animals, which not only visit the shores frequently, but often die there by thousands, as may be seen by their skeletons scattered over the guano.

109. The chemical composition of guanos. — The frequent, penetrating odor of guano is due to the presence of ammonia and of certain organic acids. Guano consists chiefly of uric acid, oxalic acid, fatty acids, resinous matter, guanin, organic matter rich in sulfur, phos-

	Per Cent
Total nitrogen	16.34
Ammonia already formed	14.08
Tricalcium phosphate	32.30
Potash	1.94
Lime	5.11
Magnesia	3.69
Sulfuric acid	0.62
Chlorin	1.04
Soda	0.54
Iron oxid	0.18
Sand and silica	1.45
Water	17.13

phoric acid united with lime and magnesia, ammonium sulfate, potassium sulfate, sodium chlorid, potassium chlorid, silicic acid, and sand. The table on the opposite page is an analysis of guano by Karnrodt.

Guano differs widely from the dung of domestic fowl in its greater percentages of nitrogen and of phosphoric acid. This is caused by the fact that the sea-birds live exclusively on fish, which are rich in nitrogen and in phosphate of lime, whereas the food of domestic birds consists chiefly of cereals, which are relatively poor in these ingredients.

110. Chemical composition affected by climatic conditions. — The great variations in the composition of guano are due to the widely varying climatic conditions to which it is exposed. In a practically rainless climate the naturally moist excrement dries quickly without undergoing material decomposition, in consequence of which its natural content of nitrogen and of phosphoric acid is still further increased. Such guanos usually contain from 12 to 15 per cent of nitrogen and from 12 to 15 per cent of phosphoric acid. The next poorer group generally ranges in nitrogen from 5 to 7 per cent and in phosphoric acid from 15 to 20 per cent. Finally, there is a group with from 3 to 5 per cent of nitrogen and from 20 to 25 per cent of phosphoric acid. In regions of occasional rainfall the nitrogen, which in the excrement is chiefly in the form of uric acid, is changed by the action of microörganisms very largely into ammonia and ammonium salts, which are readily leached away, together with the potassium salts. In consequence, there finally results a guano having a very low percentage of nitrogen and a high percentage of phosphate of lime, such, for example, as the Baker and Mejillones guanos. In humid regions

the process even goes so far that the nitrogeneous materials are not only entirely removed, but in some cases a considerable part of the phosphoric acid undergoes solution and subsequent transformation into phosphates of iron and aluminum, as, for example, on the island of Redonda.

111. Color and physical character. — The color of guano is grayish-brown to yellowish-brown, the upper layers being lighter and the deeper ones darker, the intensity increasing usually with the depth.

The physical character of guano varies more or less in different localities.

112. Chincha Island guano. — The Chincha Island guano is said to be quite uniform and somewhat pulverulent, but it contains many irregular pieces and lumps ranging from three to four inches in diameter down to particles no larger than rape seed. These lumps, which are whitish, grayish-white, reddish, or brownish, may have a dull, crumbling, fatty, or crystalline appearance. They are essentially concretionary in character, and from their analysis it appears that they consist of potassium sulfate; of ammonium, sodium, and potassium phosphates; calcium sulfate, ammonium urate, ammonium oxalate, nitrogenous organic matter, and water. Some of the lighter and softer specimens of non-crystalline character have been found to contain as much as 14.8 per cent of nitrogen. In some cases they consist chiefly of common salt and in others of ammonium phosphate. It sometimes happens, also, that small accumulations of whitish ammonium bicarbonate are found. These materials indicate the brief periodic existence of conditions favorable to decomposition, such, for example, as might be caused by an occasional slight fall of rain.

113. Significance of oxalic acid and of oxalates in guano. — The presence in guano of oxalic acid, usually combined as ammonium oxalate, is readily accounted for by the fact that it is a decomposition product of uric acid. For this reason when the uric acid content of guano is high, the percentage of oxalic acid is usually low, and *vice versa*. It was suggested by Liebig that the ammonium oxalate might be an important factor, in connection with ammonium sulfate, in effecting the solution of the tricalcium phosphate of the guano; whereby calcium oxalate and ammonium phosphate would result. This conclusion is justified, according to Heiden, only by laboratory reactions. He does not consider it likely to take place in this manner in the soil itself, owing to the absorptive property of the soil for phosphoric acid and the tendency of the latter to unite with iron and aluminum oxids, which are normal constituents of most soils.

114. Influence on the physical character of soils. — It cannot be expected that guano will have any long-continued and marked influence upon the physical character of the soil, owing not only to the small amount employed per acre, but also to the nature of the organic matter which it contains. In this respect guano greatly resembles human excrement.

115. The distribution and sources of guano. — The chief source of guano has been the mainland and especially a number of islands near the coast of Peru. These guanos have been called Peruvian guanos, or else they have received special names signifying the islands or the locations on the coast from which they were obtained. Prominent among these islands are the Chinchas, Guanape, Balestas Lobos, Potillos, and Macabi. Some of the principal points on the mainland from which guanos have

been procured are Chipana, Huanillos, Pabellon de Pica, Punta de Patillos, and Punta de Lobos. The many other islands and inland points from which guano has been secured are far too numerous to permit of their enumeration.

From the shores and islands of Venezuela, Ecuador, and Colombia, guano was exported at an earlier date under the name of Colombian guano. Prominent among these guanos were the "Monks" and "Maracaibo" guano, from the coast of Venezuela, and the "Galápagos" guano from the island of that name off the coast of Ecuador.

From Bolivia (now a part of Chili) came the Bolivian or Mejillones and several other guanos.

Guano is found on the islands of Roza and Patos on the coast of Mexico and California, and in the Gulf of Mexico on the islands of Curaçoa, Aruba, and Navassa; also in the West Indies and in Labrador. On the west coast of Africa guano is found in a number of places, one of the best known of which is the island of Ichaboe (Itschabo); it occurs also in Australia, Asia, and between China and Japan, likewise at several points in Europe, on the Jarvis and Baker islands, as well as on a large number of islands belonging to other groups in the Pacific Ocean.

The size of some of these islands is very small. For example, Baker Island is only 1914 yards long by 1210 yards wide, and it is less than 25 feet above sea level. Jarvis Island is but 1870 yards in its greatest dimension and but 1487 yards in the other, and it is but 30 feet above sea level. These islands are nevertheless visited by enormous numbers of birds, prominent among which are various species of *Pelacanus*.

Recently, after supplying the needs of Cape Colony, there have been occasional exportations of Ichaboe guano. The material, however, is that which has been deposited within the limits of a year and contains many undecomposed feathers. Its nitrogen content is about 8 per cent, but it contains less phosphoric acid than similar grades of Peruvian guano; it is also not so free as the latter from foreign matter. In recent years considerable guano ostensibly from the Chincha group of islands and from the island of Lobos has been imported into the United States, doubtless from the accumulations of recent years.

116. Adulteration of guano. — In the early days of the trade in guano, many unprincipled middlemen found it highly profitable to adulterate it. The following are some of the materials which were employed for this purpose: viz. water, carbonate of lime, gypsum, magnesium sulfate, sawdust, rice meal, common salt, sand, yellow loam, and other materials of such a character as to prevent their easy superficial recognition. In some cases low-grade guano was mixed with the good grades. Owing to the fact that there was at the outset no official inspection of such materials, the way of the transgressor was exceedingly easy.

117. "Rectified" or "dissolved" guano. — When guanos are shipped to countries having a humid climate, there is more or less danger, especially in the case of those very rich in nitrogen, that they will absorb sufficient moisture to induce fermentation and the formation of ammonia. In the course of shipment, also, cargoes frequently become moistened by sea-water with the result that the urates become more or less broken down, a change accompanied by the formation of ammonium carbonate, which then undergoes ready dissociation, and consequent

loss of ammonia. In recognition of this loss and the lesser value of such guano, its sale was for a long time forbidden under the regulations of the Peruvian government. In consequence, enormous quantities of it accumulated on the docks, especially at Hamburg and Rotterdam.

Another reason for suppressing the sale of the damaged guano was that the importers, whose trade depended upon maintaining a high grade, hesitated to throw the damaged product into the hands of middlemen who would have been likely to sell it for, and in competition with, the uninjured material; thus destroying the confidence of consumers and demoralizing the market.

In 1864 Ahlendorff & Co. made a contract with the importers to handle this discarded material, and it was dried by a process which was said to accomplish the retention of the ammonia. Soon after, this process was replaced by treatment with sulfuric acid, and for the first time in the history of the sale of guano this firm offered it under a fixed guaranty of nitrogen and phosphoric acid. This treatment not only resulted in conserving the ammonia, but it also increased the availability of the phosphoric acid. Both of these factors, and the definite assurance as to its composition, together with the frequent adulteration of the raw guano, soon resulted in its nearly driving the raw guano from the market, and the demand for the " rectified " product grew rapidly.

118. The manner of using guano. — Owing to its ready decomposition and the consequent danger of losing ammonia, the raw guano is better adapted for use where it can be incorporated with the soil at the time of its application, than as a top-dressing for grass or other growing crops. The rectified guano is ideal, for the last-mentioned purpose, for the reason that its ammonia is

fixed by union with sulfuric acid, and much of the phosphoric acid is also capable of being readily dissolved and carried into the soil.

119. Guano a poorly balanced manure. — Such guano as is found in rainless regions is especially adapted to agricultural needs for the reason that it contains not only all three of the so-called essential elements, but, in addition, lime, magnesia, iron, sulfuric acid, and other ingredients also occasionally of agricultural value. It is nevertheless true that the proportion of potash is often too low to give the best results, for in the high-grade guano of the Chincha group of islands, which contains about 12 to 16 per cent of nitrogen and 9 to 12 per cent of phosphoric acid, the content of potash ranges only from about 2.25 to 3.5 per cent. In the case of such guano, also, the ratio of phosphoric acid to nitrogen is too low to make the most economical and best-balanced manure for certain crops and soils. Again, the Lobos guano frequently contains as much as from 24 to 27 per cent of phosphoric acid and as little as from 2 to 3 per cent of nitrogen, with even less potash than is contained in the Chincha guano; hence it is obvious that considerable additions of nitrogen and potash must be made in order to make it an ideal fertilizer for most crops and conditions.

120. Bat guano unlike Peruvian and other guanos. — The so-called bat guano should not be confused with Peruvian guano, since, on account of the character of the food of the animal producing it (a mammal), it differs widely, even under the most favorable conditions, from the guano produced by birds living exclusively on fish.

121. Appearance of bat guano. — The fresh excrement of the European bat resembles in form that of the mouse, but it is not so compact, and it presents a glistening appear-

ance on account of the presence in it of undigested insect wings and other residues. Bat guanos are usually pulverulent and are ordinarily quite dry and odorous; sometimes, however, they occur as heavy, doughy, inodorous masses.

122. Where bat guano is found. — The bat is a voracious eater and hence accumulates large quantities of dung in caves, grottos, church steeples, and similar dark and obscure places to which it can gain access.

123. Chemical composition of bat guano. — The fresh dung is said by Hardy to contain about 60 per cent of water, but in bat guano the amount of water usually ranges from 12 to 25 per cent. The content of nitrogen may range from 1 to 12 per cent, the greater portion of it being present in ammonium salts associated with small, or occasional large, quantities of nitrates and more or less nitrogen in organic matter. The quantity of phosphoric acid is also widely variable, the minimum being about 2.5 per cent, and the maximum about 16 per cent. The presence of large amounts of nitrates, in some cases, is attributed to the material having rested on limestone rock at points where there is ready access of air and at least a fair amount of moisture. Like all such materials, they often contain considerable earthy matter.

124. Distribution of bat guano. — Deposits of bat guano are widely distributed in North America, the West Indies, Spain, Sardinia, France, the islands of the Indian Ocean, and elsewhere. Some of the most extensive deposits in the United States have been found in Texas and Arkansas; a single deposit in some of these cases amounting to as much as 20,000 tons.

125. Precautions in the use and purchase of bat guano. — From what has preceded it will be seen that bat guano

varies as widely in composition as the ordinary guanos from the rainless and more or less rainy regions. The best specimens approach in nitrogen content the Chincha and other high-grade guanos, whereas the poorest contain even less nitrogen than the Lobos guano. The usual amount of phosphoric acid present is from 3 to 7 per cent, although it sometimes reaches an upper limit of 16 per cent, as, for example, in a quite fresh deposit in Arkansas. The content of potash is usually very low, rarely exceeding 2 per cent, and it is frequently less than 1 per cent. The following are averages given by Goessmann: —

	Average of Nine Samples of Bat Guano from Texas	Average of Two Samples of Bat Guano from Florida
Nitrogen	6.47	9.74
Potash	1.31	1.77
Phosphoric acid	3.76	3.35

It is evident from the foregoing that such guano should be bought and sold solely on the basis of its chemical analysis.

126. Bat guano needs supplementing. — In most cases these guanos must be supplemented by applications of potassium salts and by readily available phosphatic fertilizers, if they are to be used in the most economical way.

CHAPTER VIII

FISH, CRAB, LOBSTER, AND SIMILAR WASTES

The term "fish guano" is often applied to fish and fish wastes, but since it is in no strict sense guano, as implied by the Spanish origin of the name, it is more properly considered under a separate chapter.

127. Fish long used as a fertilizer. — The use of fish and of fish waste as a fertilizer by people living near the ocean, or wherever fisheries flourish, has long been practiced. In fact, the American Indian was no exception, for he had already learned to apply fish as a fertilizer for his maize when the Europeans first landed on the shores of North America.

128. Early catching of fish for fertilizer purposes. — As early as 1872 the catching of fish, which were employed for fertilizing the soil for both wheat and hops, had become quite an industry on the coasts of Essex, Kent, and Sussex, in England. The fish, which were very small, were a variety of herring (*Clupea sprattus*). They were subjected to a stamping and crushing process and were applied to the soil without further preparation.

129. Special processes for preparing fish for fertilizer uses. — In 1853 Petlitt patented a process for the preparation of a fertilizer from herring. The nitrogen content of this prepared material ranged from about 11.2 to 13.8 per cent.

Shortly after the middle of the preceding century Ch. de Molon, who had already convinced himself by

practical trials on his estate on the coast of Brittany of the manurial value of the wastes from the sardine fisheries, conceived the idea of treating the material in such a way as to prevent its rapid decomposition and render it transportable to long distances. To this end De Molon associated with himself Thurneyssen, and they erected a factory near Brest, in which to carry out the process. This, in brief, consisted in heating the fish with steam applied between the walls of a double-walled kettle at a pressure of three and one-half atmospheres (140° C.), after which it was pressed. In this process the amount of oil recovered from the top of the waste liquors represented about 2 to 2.5 per cent of the fresh fish. The waste liquors, because of their high nitrogen content, sometimes created a nuisance, on which account they were often evaporated, whereby the solid matter was saved. The remaining cake was passed through a machine which rubbed it into a thick dough, in which state it was taken to the drying room and subjected to a temperature of from 48° to 56° R., until it was ready for grinding, in final preparation for shipment. The dry product ready for marketing represented about 22 per cent of the original weight of fish.

130. Fish wastes in Japan. — In Japan herring are likewise utilized for the manufacture of oil and fish-scrap, the latter being used without further manipulation, in fertilizing tea plants, tobacco, cotton, and other crops.

131. Fish wastes in Newfoundland. — In connection with the Newfoundland cod fisheries, the heads, entrails, bones, and other waste portions of the fish, to the amount of 700,000 tons annually, were cast into the sea until De Molon sent his younger brother to the Island to erect a factory for the preparation of fish guano for export.

132. Norwegian wastes from cod and whales. — In Norway fish guano is prepared from the wastes of the cod-fishing industry and from whales. The number of cod-fish said to be taken annually in that country amounts to from 18,000,000 to 20,000,000. A considerable number of factories are engaged in the preparation of the waste for fertilizing purposes. The finished product has a white to brown color and usually contains from 8.5 to 11 per cent of water, 8 to 10 per cent of nitrogen, and 12 to 14 per cent of phosphoric acid.

133. Methods of handling Menhaden in the United States. — The method of handling the Menhaden (a sort of herring also called pogys, *Alsa menhaden*) now practiced in the United States, varies somewhat in the different works. In some places the former method of unloading from vessels by means of tubs holding $3\frac{1}{2}$ barrels, or about 1000 fish, is still in vogue. By that method from 80,000 to 100,000 fish can be discharged per hour. The tubs are raised by means of a steam hoister installed on the steamer and used in raising to the deck the fish caught in the seines. In certain instances, also, they are raised by hoisters located at the dock. From the tubs the fish are passed to a receiving box, from which they are taken into cars. They are then hauled up an inclined track by another hoister and delivered into wooden vats, well provided with steam pipes. Each of these vats holds about 20,000 fish. Here they are cooked until they are ready for pressing in powerful hydraulic presses which leave a product containing from 50 to 60 per cent of moisture. The scrap is then either treated with sulfuric acid, in order to prevent its decomposition, or it is sun-dried on platforms. At present most of the factories are equipped with elevators which transfer the fish to the receiving boxes and conveyors at

the rate of 250,000 or more per hour, for each elevator in operation. From the elevator the fish are carried into iron cookers of various sizes, which are from 20 to 30 feet long, and from 2 to 3 feet in diameter. The fish pass through these cylinders, subjected to a continual steam pressure of 100 pounds to the square inch, at the rate of from 100,000 to 150,000 per hour; they then pass, by a conveyor, directly into screw presses of various sizes. The larger presses now in use have a capacity of 150,000 fish per hour. Upon leaving the presses the scrap is carried, largely by means of conveyors of various types, to the acidulated scrap storage or to the dryers, as desired. In some cases the scrap is treated with sulfuric acid and is then transferred directly to vessels lying alongside of those which are discharging the fish.

134. Fish waste treated with sulfuric acid. — Attempts have been made to treat the fish waste with considerable quantities of sulfuric acid, but this has proved to be a very difficult operation; and in but few instances is the character of the fish products such that this treatment is considered practical. The amount of water in such treated material may range from 13 to 18 per cent, the total nitrogen from 7 to 9 per cent, and the total phosphoric acid often from 11 to 12 per cent. By this treatment two-thirds of the phosphoric acid is rendered immediately soluble in water. A part of the nitrogen may be changed into ammonia, and, under the usual conditions, about one-third of it is thus changed.

135. Chemical composition and utilization of whale products. — Fresh whale-meat contains about 44 per cent of water, 23 per cent of fat, 32 per cent of flesh, and 1 per cent of ash. In its undried condition it contains about 4.8 per cent of nitrogen, but when fully dried the nitrogen

content is about 8.7 per cent. The whale-bone, with a content of 3.84 per cent of water, contains 1.3 per cent of fat, 34.6 per cent of organic matter, and 60.2 per cent of ash. The nitrogen amounts to 3.5 per cent. In the manufacture of fertilizer from the bones and meat of whales, the fat content is so great that many difficulties are met in making the separation. The whale glue which is unfit for other purposes finds its way into fertilizers. It contains approximately 8.4 per cent of nitrogen and 3.2 per cent of phosphoric acid. Whale flesh, when dried and freed from fat, contains from 14 to 15 per cent of nitrogen. A so-called " whale guano," with from 7 to 8 per cent of nitrogen and 9 to 10 per cent of phosphoric acid, and whale-bone meal with 4 per cent of nitrogen and 21 per cent of phosphoric acid, have been offered in the market.

136. Availability and use of fish guano. — The availability of the nitrogen of fish guano stands close to that of dried blood. Like all such organic nitrogenous materials, the nitrogen is not so quick in its action as that in nitrate of soda, potassium nitrate, or even in sulfate of ammonia. There are several important conditions upon which its transformation into nitrates and its consequent efficiency very largely depends; as, for example, the temperature, moisture, soil reaction, the fungi, and the bacterial flora of the soil. Because of the several conditions necessary to the transformation of the nitrogen of such materials into ammonia and eventually into nitric acid, it is usually best to incorporate it with the soil rather than to use it as a top-dressing. Though not absolutely necessary, it is desirable that fertilizer ingredients of this character, if applied in large quantities, should be incorporated with the soil several days before the seed is planted. In this way possible injury to the plant seedlings, which

might arise in connection with the processes of fermentation, may be avoided.

137. Fish guano requires supplementing. — Owing to the high percentage of nitrogen present in fish guano, it should usually be applied in conjunction with bone, or preferably with basic slag meal or with acid phosphate, or other superphosphates. It is usually important, also, that it be properly supplemented with suitable potassium salts.

138. Fish scrap may be employed without further treatment. — As a rule the fish scrap is sold directly to fertilizer manufacturers, but whenever it and the waste untreated fish or parts of fish are obtainable at low cost, near where they can be utilized, they can be employed advantageously by spreading them on the surface of the land and plowing them under as one would use stable manure.

139. The value of fish waste depends on the climate and soil. — It is reported by Kellner that in certain parts of Japan fish scrap, owing to the warm climate, moisture, and other conditions favorable to decomposition, is a quick-acting fertilizer; but in very cold countries, where the reverse conditions prevail, its action is slow and is especially unsatisfactory early in the spring. For many reasons such material is much better adapted for use on sandy or naturally open soils than on compact silts and clays.

140. Shrimps. — Along the coast of the North Sea there are found millions of shrimps (*Crangon vulgaris*), which, though prized as a great delicacy for human food, are used at times in great quantities in the manufacture of fertilizer. Since the product is relatively poor in phosphoric acid, it is often supplemented by additions of bone or of other phosphatic fertilizers.

141. The king-crab. — In the United States the king-crab (also known as horse-foot or horse-shoe; *Limulus Americanus*) has not only been utilized directly as a fertilizer, but it has also been dried, ground, and sold under the name of "horse-foot guano." It has often been used as an ingredient of various commercial fertilizers. In a dry state this material contains, as found by Voorhees, about 10 per cent of nitrogen, which apparently possesses a high degree of availability. According to Storer, it is necessarily poor in phosphoric acid, as is shown by the fact that the dried shells, after being freed of the flesh attached to the upper portions and to the legs, contained but 0.26 per cent of phosphoric acid. They contain only 0.06 per cent of potash, but the content of nitrogen has been found to be equal to as much as 12.55 per cent.

142. The common crab. — According to Storer, the common crab (*Lupa dicantha* Milne-Edwards) collected on the shore of Massachusetts was found to contain 3.6 per cent of phosphoric acid, 0.2 per cent of potash, and 1.95 per cent of nitrogen.

143. Lobster refuse. — The shells of cooked lobsters (*Homarus Americanus* Milne-Edwards), are reported by Voorhees as containing, when dry, an average of 3 per cent of phosphoric acid, 20 per cent of lime, and 4 per cent of nitrogen. An analysis of lobster shells reported by Goessmann, shows that they contained 7.3 per cent of water, 4.5 per cent of nitrogen, 3.5 per cent of phosphoric acid, 22.2 per cent of lime, and 1.3 per cent of magnesia.

144. Star-fish. — In the case of fresh star-fish examined at the Rhode Island experiment station it was found, after rinsing with fresh water and removing the superficial moisture, that they lost, upon drying, 64.4 per cent of their weight. The mineral matter remaining after they

were incinerated, amounted to 20.3 per cent. The fresh undried star-fish contained 9.62 per cent of lime, 0.23 per cent of potash, 0.20 per cent of phosphoric acid, and 1.8 per cent of nitrogen. The value of these ingredients in a ton of fresh star-fish, based upon the recent ruling prices for lime and the other ingredients, would range from about $6 to $7.50 per ton.

It is reported that on the French and Belgian coasts of the North Sea a mixture of certain mollusks with star-fish is employed as a manure, under the name "Coquilles animalisées."

CHAPTER IX

COMMON SLAUGHTER-HOUSE NITROGENOUS WASTE PRODUCTS

THE number of waste nitrogenous animal substances is so large, and they are so important, that they demand individual mention.

145. Dried meat meal. — Among the trade names which have been applied to various preparations of dried meat meal are "animal matter," "dried meat," "azotin," and "ammonite." These materials are produced in the process of rendering dead animals, meat refuse, and as a waste product from the manufacture of meat extract. In the preparation of such extracts much of the phosphoric acid is removed, on which account certain Australian products have been placed on the market mixed with bone meal. These contain about 6 per cent of nitrogen and about 13 per cent of phosphoric acid.

The rendering process. — In the rendering process refuse bones and meat are placed in steel tanks where they are subjected for a few hours to a steam pressure of from 40 to 60 pounds, or higher. As a result of this treatment the fat is separated and the bones are rendered highly friable, in consequence of which they can be easily ground. After the removal of the hot liquors the fat rises to the surface of the liquid, where it solidifies upon cooling; the meat is also separated from the bones, after which it is dried and ground.

146. All readily utilized by fertilizer manufacturers. — Before the manufacture of fertilizers had grown to its present proportions, these meat residues were readily available to the farmer, but now that the supply fails to keep pace with the demands, the manufacturers of " complete " fertilizers readily absorb the entire supply.

147. Chemical composition of meat meal. — The amount of nitrogen in the best of the meat meals ranges usually from 13 to 14 per cent; though they may contain as little as 10 per cent, according to the amount of impurities and moisture present. In addition to nitrogen the meat meals contain varying percentages of phosphoric acid, depending in amount upon their origin and the quantity of bone associated with the meat.

148. Availability of meat meal. — In the availability of their nitrogen, these waste meat materials stand, according to Wagner, somewhat behind dried blood, horn meal, and tender plants, and on about the same plane as nitrogen in fish guano, bone, and bone tankage; hence they stand in the next to the best group of organic nitrogenous manures.

149. The nature of bone tankage. — Bone tankage consists of rendered or steamed bone associated with a considerable quantity of meat, cartilaginous matter, and other substances. It is prepared from the animal refuse secured from slaughter-houses and meat markets.

150. Composition of bone tankage. — Its nitrogen content may range from 4 to 12 per cent and its content of phosphoric acid from 7 per cent to approximately 20 per cent. In the United States six commercial grades are often recognized with 18, 16, 13.5, 11.5, 9, and 7 per cent as the respective minimum percentages of phosphoric acid. It is obvious that these are mere arbitrary subdivisions,

and that any one grade must range up to the next higher just as the highest of the bone tankages range up to the minimum of what is recognized in the trade as bone.

151. Value of bone tankage as a fertilizer. — The value of bone tankage as a fertilizer depends to a considerable extent upon its degree of fineness. The importance of this feature is greater, the larger the quantity of bone, and consequently the higher the percentage of phosphoric acid. It is probable that the fertilizing value of the nitrogen in bone tankage does not differ materially from that in bone, fish, and meat meal, and it should logically stand between the first two.

152. Method of employment. — The best method for the employment of bone tankage is to introduce it into the soil in finely ground form, rather than to use it in a coarse condition or to employ it as a top-dressing.

153. Chemical composition of red dried blood. — The red dried blood, which differs from the black blood in its method of preparation, possesses ordinarily the higher commercial value, and usually contains from 13 to 14 per cent of nitrogen, though if imperfectly dried it may contain much smaller percentages.

154. Chemical composition of black dried blood. — Black dried blood as commonly offered in the market may range in nitrogen content from 5.5 to 12 per cent, and especially good lots have been found to contain over 13 per cent.

155. Reasons for occasional low nitrogen content of blood. — The low content of nitrogen sometimes found in dried blood may be due to the incidental or intentional introduction, in the course of its handling and manufacture, of more or less bone and tankage. It may also be due to its adulteration with pulverized roasted leather,

pulverized peat, or other substances, the detection of which, by casual inspection, and even in some cases by chemical or other means, has heretofore been difficult or impossible. If the blood contains much tankage or bone, there will be much more phosphoric acid present than the small quantity normally associated with pure blood.

156. Chemical composition of the better commercial blood. — The better grades of commercial dried blood usually contain from 13 to 14 per cent of water, from 10 to 13 per cent of nitrogen, 0.5 to 1.5 per cent of phosphoric acid, and from 0.6 to 0.8 per cent of potash, though it is ordinarily sold without reference to anything but its nitrogen content.

157. Crystallized blood. — What is known as "crystallized" dried blood is produced by evaporation at a temperature of about 60° C., and it is capable of being redissolved. Owing to its cost, it is usually employed for industrial rather than fertilizing purposes.

158. Certain processes of preparing dried blood. — In the process of transforming blood into the dried marketable material, it is agitated vigorously and is at the same time treated with steam in a vessel with a perforated false bottom. As a result of the raised temperature, coagulation of the fibrin and albumen takes place, after which the slightly reddish liquid portion is withdrawn. After drying, the blood is milled to a proper degree of fineness. The yield of dried blood is above 20 pounds per 100 pounds of the original material. The coagulation is often hastened by the addition of a small amount of concentrated sulfuric acid. Sometimes from 2 to 3 per cent of pulverized quicklime is added to the blood before flocculating. In consequence of this addition, any ammonia in the waste water is disengaged, and the material can then be dried in

the air, if desired, with the result that a practically odorless fine powder is produced.

If blood is allowed to stand for some time, after adding from 1.3 to 3 per cent of lime, the mass will solidify and can be subsequently air-dried with ease and without undergoing decomposition.

In the process of drying and preparing dried blood, a mixture of iron sulfate, sulfuric acid, and sodium nitrate is often added. The coagulation in such cases is very rapid, and the material gives off no bad odors during the process of drying. It is not practical for this purpose to use solely the commercial iron sulfate, for if this is done there results a pasty mass which does not dry readily. In order to obviate this difficulty, a mixture of sulfate of iron and of alum is sometimes employed; also treatment of the blood with calcium carbonate (chalk) and peat; and precipitation with alkaline sulfates or phosphates and acid ferric sulfate.

159. Dried blood, if very fine, is highly hygroscopic. — The finer the blood is ground, the more hygroscopic it becomes, and when made excessively fine the water content has been known to reach 27 per cent. This high moisture content is, however, not desirable in material which must be stored, for too much moisture is likely to lead to changes resulting finally in a loss of ammonia.

160. Availability of blood dependent upon soil conditions. — Dried blood is the best, or one of the best, organic nitrogenous fertilizers, but like others it is dependent for its efficiency upon the character of the soil. This is well shown by experiments made with it on upland silt loam soil, at the Rhode Island experiment station, in which the availability of the nitrogen in an excellent lot of black dried blood, containing slightly over 13 per cent of nitro-

gen, was considerably less than one-half as great as in nitrate of soda, whereas after liming the soil, the availability of the nitrogen rose to over 90 per cent of that in nitrate of soda.

161. Processes of preparing horn meal and hoof meal. — In the various manufacturing establishments where horn is employed, there is a large lot of waste material. The preparation of such horn waste, and of hoofs, for fertilizing purposes, is sometimes accomplished by subjecting them for about twelve hours to steam pressure, after which the material is dried and ground to a fine powder. It is then sold as horn meal and hoof meal. Another method of manufacture is to subject the materials to high temperatures, even frequently to the extent of slight roasting, after which they can be easily pulverized. In consequence of the loss of water in this process the nitrogen content is raised materially.

162. The chemical composition of horn meal. — A very pure sample of horn meal is reported as containing 9.5 per cent of water, 87.4 per cent of organic matter, and 1.69 per cent of ash, in addition to small amounts of impurities.

The amount of nitrogen present in horn (in keratin) is about 14.1 per cent, phosphoric acid 0.28 per cent, and lime 0.48 per cent.

Certain English writers report the range of nitrogen in commercial samples of horn meal to be from 7 to 15 per cent.

163. Chemical composition of horn and hoof meal. — A sample of mixed horn and hoof meal, from a lot in which hoofs were used which had a small amount of bone adhering to them, was found by C. Peterson to contain 13 per cent of nitrogen and 5.5 per cent of phosphoric acid.

Samples are reported from France as containing from 16 to 17 per cent of nitrogen. The analyses of three different lots of hoof and horn meal are reported by Goessmann in which the minimum of nitrogen was 11 per cent and the maximum 15.5 per cent.

164. The nitrogen content of hoof meal. — The average nitrogen content of hoof meal is generally held to be about 12 per cent.

165. The efficiency of hoof meal. — Hoof meal in its natural condition is held by Voorhees, Murray, and others as being of little value, even though finely ground; and some authorities assert that even after steaming, the value of the nitrogen is still far below that in blood and tankage. It is nevertheless superior to leather, wool waste, and hair, and Heiden ranks it as a very effective nitrogenous fertilizer (Düngerlehre, *2*, 746).

166. The adulteration of horn and hoof meals. — It is reported that horn meal and hoof meal are sometimes adulterated with ground nut shells and other difficultly recognizable sustances. On this account, in purchasing such materials, one should buy only on the basis of a guaranteed analysis. The adulteration may explain much of the discordant testimony as to the agricultural value of these materials, for it does not appear that the genuineness of the lots employed in certain experiments was always determined.

167. Preparatory treatment of waste leather. — Large quantities of leather waste are now said to be employed in the manufacture of ready-mixed fertilizers. In its preparation for such use a wet acid or " chamber " process, involving a simultaneous treatment of raw phosphates, is applicable, as it is under certain conditions to many of the other waste nitrogenous materials. Waste leather is

also treated with steam, in the same way as hoof meal and horn meal. It is then dried and ground, or in lieu of steaming it is often roasted and ground. The value of such prepared leather, unless it is subjected to the " chamber " process, is very small in any case, although it is slightly greater if steamed than if roasted. Owing to the destruction of the tannin in the roasting process, the leather thus prepared is said to be selected as an adulterant of dried blood and of certain other high-grade nitrogenous substances, on account of the difficulty of its recognition.

168. The chemical composition of prepared leather waste. — The leather meal prepared by the steaming or roasting processes contains from 7 to 9 per cent of nitrogen and from 0.5 to 1 per cent of phosphoric acid; although it may sometimes range slightly above or below these figures.

169. The availability of nitrogen in leather. — If employed on a soil in which the conditions for nitrification are poor, the value of the nitrogen of roasted leather may be even less than one-hundredth as great as that of the same quantity in nitrate of soda; if, however, the conditions for nitrification are ideal, its value may rise to from 13 to 20 on the basis of 100 for the nitrogen in nitrate of soda. At all events, such leather is one of the least valuable of the nitrogenous fertilizers. It is obvious, therefore, that roasted or steamed leather meal, if employed directly as a fertilizer, is not worth the cost of transporting to very great distances. It is, however, probable that by the sulfuric acid or " chamber " process a considerable part of the nitrogen is changed into sulfate of ammonia and that the organic residues remaining are also rendered still more available to plants.

170. Treatment of leather with carbonates of the alkalies. — It has been proposed by Reichardt to treat waste leather with carbonates of the alkalies. Before being subjected to such treatment, powdered leather was found to be soluble in hot water to the extent of but 15.8 per cent, but after being left in contact with a 5 per cent solution of sodium carbonate for several days, it was soluble to the extent of 28.8 per cent. This method of treatment has, however, apparently never found any extensive application in practice.

171. Leather really not so valuable as it appears. — The inefficiency of the nitrogen in leather meal, as compared with that in the better class of nitrogenous materials, is not shown adequately by merely the smaller weights of the resultant crops, since crops grown with the aid of an abundance of readily available nitrogen are often richer in that element, and hence possess a greater feeding value than those grown with poorer and less available materials, like leather. This is well illustrated by experiments by S. W. Johnson in which nitrogen in blood, at the rate of 20 pounds per acre, gave four times as great an increase in crop as the same amount of nitrogen in horn. The increase of nitrogen in the crop was also nearly twice as great in the former as in the latter case. With 40 and 60 pounds of nitrogen per acre, the same principle held true, although the proportionate increases were not the same as in the first instance.

CHAPTER X

OTHER MISCELLANEOUS NITROGENOUS SUBSTANCES

A CONSIDERABLE number of plant residues and of other miscellaneous materials of somewhat uncommon occurrence are often used for manurial purposes. These will now be considered.

172. Feathers. — Clean feathers, according to the analyses of Payen and Boussingault, contain 15.3 per cent of nitrogen. The sweepings from a feather warehouse, however, contained but 6.25 per cent of nitrogen, indicating the presence of much foreign matter.

Feathers decompose slowly in the soil, and hence they have a small positive value as a fertilizer, even without special treatment.

173. Hair bristles and wool. — The hair of various animals, the bristles of swine, and wool all contain essentially the same amounts of nitrogen as feathers. In other words, if free from all impurities, they contain from 14 to 15 per cent of nitrogen. After drying at 250° F., human hair has been found to contain 17 per cent of nitrogen.

174. Tannery hair. — Hair from tanneries contains more or less foreign matter and water, which lessen the nitrogen content. The amount of nitrogen found in such hair ranges from 5.5 to 8 per cent, the average being about 6.5 per cent. Certain of the calcareous wastes of the tanneries, charged with organic matter derived from the cleans-

ing and preparation of hides, contain from 2.8 to 3.4 per cent of nitrogen.

175. Waste silk. — The nitrogen content of waste silk and silk rags ranges from 8 to 11 per cent of nitrogen, depending upon the purity of the materials.

176. Wastes from hares and rabbits. — In the preparation of the hair of hares and rabbits for the manufacture of hats, the ears, tails, legs, and irregular parts of the skin often accumulate in considerable quantities as waste matter. This material, according to C. Thiel, has been found to contain 7 per cent of nitrogen, 0.6 per cent of potash, and 1.7 to 3.1 per cent of phosphoric acid.

177. Chemical composition of waste wool. — Wool waste may contain from 0.5 to 7 per cent of nitrogen, dependent upon the amount of water and of foreign matter which is present. The range in the water content is usually from 15 to 50 per cent. Various methods have been proposed for utilizing this and other nitrogenous materials.

178. Wool waste as a manure. — Wool waste has long been used in its natural condition as a manure for hoed crops and in preparation for seeding to grass; and, like coarse stable manure, it is best to spread it broadcast and turn it under with a plow. Its use is seldom to be recommended, excepting where the transportation charges and the cost of application are small.

179. Effect of superheated steam on wool waste. — When wool waste is subjected to high steam pressure, it assumes a liquid condition. Upon subsequent evaporation there remains a dark brown powder said to be very largely soluble in water and supposed to consist of leucin ($C_6H_{13}NO_2$), tyrosin ($C_9H_{11}NO_3$), and other related amid compounds.

180. Concerning Petermann's tests of availability. — Experiments by Petermann, conducted in the field and in pots, have appeared to show that notwithstanding that the nitrogen of wool is rendered more available by the process of steaming, it is still much inferior to nitrogen in nitrate of soda. These experiments were made with spring wheat and with beets in conjunction, in certain cases, with phosphates, but without potassium salts. It is interesting, in view of the omission of potash, to note that the nitrogen in nitrate of soda appeared to possess relatively greater superiority for the beets than for the wheat. This, in the light of observations made by Hellriegel, Wilfarth and others in Germany, and by Wheeler and Hartwell at the Rhode Island experiment station, indicates a probable direct or indirect manurial effect of the soda, the first or both of which would be expected to be greater in connection with beets than with wheat. Owing to this failure to provide an abundance of potash and to recognize the possible beneficial alkaline effects arising from the residual sodium carbonate formed from the nitrate, too great value was doubtless attached to the nitrogen in nitrate of soda, and too little to the effect of steaming as a means of increasing the efficiency of the nitrogen of the wool waste.

181. Soluble wool waste not subject to loss by leaching. — It was found by Petermann that practically none of the soluble nitrogenous organic matter was lost from the soil by leaching, in which respect it possesses certain distinct advantages in open soils.

182. Benefit from steaming not equally applicable to all other nitrogenous wastes. — Attention has been called by S. W. Johnson to the fact that the availability of certain materials, such as bones, tendons, and hide,

which yield glue, may be injured by steaming, in case the glue is not removed. This is said to be due to the cementing action of the glue, on account of which the decomposition of the material in the soil is hindered; nevertheless, horn, hoof, hair, wool, and certain other materials are benefited by the treatment.

183. The production of garbage tankage. — Garbage tankage is the product derived from the treatment of kitchen wastes, and it may be composed of materials of both vegetable and animal origin. The refuse is treated with steam at high pressure, as a result of which it is completely disinfected, and much of the water is expelled. This product is then extracted by benzene, which is subsequently recovered and used for the repeated extraction of new lots of material. The extracted residue is then screened, in order to permit of the recovery of the bones and of other miscellaneous materials, in separate portions. It is said by Storer that 30,000 pounds of kitchen waste have been found to yield by this process 1800 pounds of grease and 12,000 pounds of garbage tankage. In this process the vapors are condensed and passed into the sewers, and the various operations are said to be practically unaccompanied by odors.

184. The fertilizer value of garbage tankage low. — Such garbage tankage is of rather low value as a manure. It is used by a few fertilizer manufacturers, some of whom fortunately submit it to the so-called "wet chamber" process, by which its value as a fertilizer is at least somewhat improved.

It usually contains from 2.5 to 3 per cent of nitrogen, 1.5 to 3 per cent of phosphoric acid, and from 0.7 to 1.5 per cent of potash.

185. The character of shoddy and felt refuse. — The

term "shoddy," as formerly used, referred to short fragments of wool rejected in various woolen industries. Now, however, the name is often applied to wastes of both silk and wool.

186. Chemical composition of shoddy and felt. — Shoddy usually contains from 4 to 12 per cent of nitrogen, the average content being about 6.5 per cent.

A felt refuse examined by Goessmann was found to contain 5.26 per cent of nitrogen. It may therefore be classed as of about the same general character as shoddy.

187. The use of felt and shoddy wastes as manures. — Felt and shoddy wastes are highly esteemed as a manure for grapes and certain other fruits, and especially for hops. This is supposedly due to the fact that these crops do not require a large amount of nitrogen at any given time, but thrive best where the supply, though small, is continuous throughout the season. For such purposes shoddy is considered as one of the best substitutes for farm-yard manure, and in many cases it is even chosen in preference to the manure. From 1 to 2.5 tons of shoddy are considered equal to 20 tons of farm-yard manure.

Shoddy not only exerts a direct manurial action, due to its high content of nitrogen, but it also improves very greatly the physical condition of certain soils.

188. The character of soot. — Soot consists chiefly of finely divided particles of carbon which are deposited in chimneys during the imperfect processes of combustion. On account of its finely divided physical condition, it condenses gases upon its particles to a high degree, and hence often becomes rich in ammonia which it has absorbed from the gaseous products of combustion.

189. The chemical composition of soot. — The nitrogen content of soot may range from about 0.5 to 6 per cent, the average being about 3.2 per cent.

190. Soot benefits physically. — Owing to its dark color, soot is supposed to cause soils upon which it is spread to absorb more heat, thus forcing the crop and creating conditions favorable to bacterial activity. When it is introduced into soils it also improves their physical condition, especially if they are of a clayey texture.

191. Soot rarely toxic. — A sample of soot has been reported in Europe which was found to be toxic to plants, due to the presence of pyridin or similar compounds, yet the almost universal indorsement of soot as a fertilizer shows that the presence of poisonous substances must be considered as most exceptional.

192. Light soot best. — The best soot is usually that which is the lightest in weight, and heavy weight indicates contamination with mineral matter of questionable value. The usual weight of a bushel of soot is about 28 pounds.

193. Insects and cocoons. — It has been found that certain insects yield as much as 19 per cent of fat, and that in their natural state they may contain from 3.2 to 8.41 per cent of nitrogen. In addition, the content of phosphoric acid has been found to range from 0.6 to 1.5 per cent and the potash from 0.5 to 0.96 per cent. Certain of the richer of these insects, after the removal of the fat and complete dessication, yield a product containing as much as 14 per cent of nitrogen.

The cocoons of the silk worm have been found to contain 1.82 per cent of phosphoric acid, 1.08 per cent of potash, and 9.42 per cent of nitrogen.

194. Peat and muck. — Peat and muck, though containing all of the usual mineral elements of agricultural

importance, nevertheless contain too little of any of them to be of practical significance as manures. Such vegetable residues are valuable as soil amendments by virtue of the large volume of organic matter which they contain, and on account of their nitrogen, although the latter is but very slowly available. The composition of muck and peat varies widely, dependent upon whether they are derived from trees, shrubs, grasses, mosses, or other forms of plant life and also according to the quantities and kinds of mineral matter which they contain. Air-dry peat may be assumed to range in nitrogen content from 1 to 2.5 per cent, according to the materials of which it was formed.

195. Peat and muck especially valuable on light soils. — Peat and muck are especially applicable for use on light, sandy, and gravelly soils which leach badly and lack vegetable matter. On such lands these materials may effect a veritable transformation in productiveness, especially in seasons when the rainfall is light, or when it is unevenly distributed, but not always if excessively dry.

196. Salt and fresh muds. — Dried mussel mud is reported by Goessmann as containing 0.72 per cent of nitrogen and 0.35 per cent of phosphoric acid. Another sample of salt mud, with 53 per cent of water and 41 per cent of ash ingredients, contained 0.4 per cent of nitrogen. Fresh-water mud, with a moisture content of 40 per cent, contained 1.37 per cent of nitrogen, 0.22 per cent of potash, and 0.26 per cent of phosphoric acid.

None of these materials is sufficiently valuable to justify hauling to a considerable distance, and they are often chiefly of use in improving the physical condition of sandy or gravelly soils.

197. Cereal and other seed by-products. — Among the various cereal and other seed by-products, cotton-

seed meal is probably the most important, from the fertilizer standpoint, of any which are extensively used in the United States. Notwithstanding the high feeding value of cotton-seed meal and the wisdom from the standpoint of national economy of feeding it first, and of using the resultant dung as a manure, enormous quantities of it are used separately for special manurial purposes and also as an ingredient of ready-mixed commercial fertilizers. It is used extensively, especially in the South, not only as a manure for cotton and sugar cane, but also for other crops, and it is one of the favorite sources of organic nitrogen, especially for tobacco. For this latter purpose enormous quantities of it are used in the Connecticut Valley, in the states of Connecticut and Massachusetts.

198. The composition of cotton-seed meal. — Owing to changes in the method of removing the oil, cotton-seed meal is not usually as rich in nitrogen as formerly, the lower limit for the decorticated meal being about 6 per cent, and the upper limit 7 per cent. The undecorticated cotton-seed meal contains about 4 per cent of nitrogen. In addition to nitrogen, cotton-seed meal contains about 2.5 per cent of phosphoric acid, and about 1.7 per cent of potash.

199. The composition of linseed meal. —Linseed meal and cake contain from 4.9 to 5.8 per cent of nitrogen, 1.2 per cent of potash, and 1.8 per cent of phosphoric acid.

200. The composition of malt sprouts. — Malt sprouts reach a limit of from 3.5 to 4 per cent of nitrogen, 2 per cent of potash, and 1.3 per cent of phosphoric acid.

201. The composition of castor pomace. — Castor pomace contains from 5.5 to 5.75 per cent of nitrogen, from 0.6 to 3.4 per cent of potash, and from 1.5 to 2.25 per cent of phosphoric acid.

202. The composition of wet brewer's grains. — Wet brewer's grains contain 76 per cent or more of water, 1.2 per cent of ash, 0.9 per cent of nitrogen, 0.5 per cent of phosphoric acid, and 0.05 per cent of potash.

203. The composition of gluten feed. — Gluten feed contains usually from 4 to 5 per cent of nitrogen, but only 0.75 per cent of ash.

204. The utilization of the spent wash of distilleries. — The spent wash of distilleries of various kinds contains notable quantities of nitrogen. This represents a loss of 1 to 1.25 pounds of nitrogen, per 10 gallons of 100 per cent alcohol produced. The wastes from the distillation of beet sugar, molasses, and sucrate liquors contains 1.4 per cent of nitrogen and 0.9 per cent of salts. Attempts to recover these wastes by dry distillation are complicated by the tars and other products, difficult of purification. Many other methods of treating these liquors have likewise been tested.

205. The process of Vasseux. — The process of Vasseux, which is employed with gratifying results in France and Spain, consists in concentrating the wash and adding sulfuric acid, whereupon the potassium sulfate crystallizes out in the mass and is separated by decantation, filtration, and centrifugal treatment, yielding finally a product containing 75 to 80 per cent of potassium sulfate. The drying of the liquor is completed *in vacuo*, whereupon it is poured into trucks. After cooling, this residue is crushed and prepared for agricultural use. The final product contains 6 to 7 per cent of nitrogen and 6 to 7 per cent of potash. It is almost wholly soluble in water, and is said to be an excellent fertilizer. The usual yield is 300 pounds of fertilizer per ton of the molasses treated.

206. The process of Effront. — A process devised by Effront consists in converting the organic nitrogen of these spent liquors into ammonia by the employment of amidase in an alkaline medium. The ferment is then separated for further use, and the ammonia is won by distillation. A butyric acid ferment and others separated from a garden soil have been similarly employed by Effront in treating spent wash. By this method there was secured from 814 gallons of molasses, not only the customary 22 gallons of alcohol, but also 77 pounds of pure volatile fatty acids.

CHAPTER XI

THE AVAILABILITY OF ORGANIC NITROGEN AND FACTORS AFFECTING IT

In determining the availability of organic nitrogenous substances, the efficiency of their nitrogen is usually compared with that in nitrate of soda, which for the sake of convenience is usually placed at 100.

207. The factors of temperature and moisture. — In such work temperature and moisture conditions, as well as the texture and chemical reaction of the soil, are important factors, for it is well recognized that in warm climates, especially on open soils, and for plants having a long period of growth, comparatively inert forms of nitrogen act much better than in temperate climates and on compact soils.

208. Effect on the soil reaction. — It is coming to be more generally appreciated than formerly that soils are rendered less acidic or more alkaline by sodium nitrate, whereas certain organic nitrogenous substances may exert an appreciable ultimate acidic effect upon the soil by virtue of the nitric acid resulting in the course of their decomposition.

209. Effect of large applications at the outset. — In case a very heavy application of nitrate of soda is made at the outset, it may in some cases interfere, for a time, with the physiological functions of the plant to such an extent that even if it actually takes up more nitrogen,

the total quantity of dry matter may finally be less than that produced by a like amount of nitrogen in certain organic materials, which are more slowly available. For this reason deductions as to the availability of the nitrogen should properly be based upon the nitrogen actually taken up by the plants, rather than merely upon the total dry matter produced.

210. Employment of different amounts of nitrogen. — It is also important in making such availability tests to use two or three series of experiments in which different amounts of nitrogen are employed.

211. Other elements must be supplied generously. — Care should also be taken to determine definitely by experiment whether enough of all the other fertilizing ingredients has been employed to insure that nitrogen is really made the factor which limits growth. The point just mentioned is especially important in view of the now well-recognized physiological and other functions, performed by sodium salts when potash is lacking, for if the supply of potash were insufficient, the greater yield produced by nitrate of soda, in comparison with organic nitrogen, might be due to a considerable extent to the soda having performed some part of some of the functions of potash. If this were not guarded against or anticipated, the conclusion might be drawn that the nitrogen in other materials was relatively much more inferior in comparison with that in nitrate of soda than the actual facts would justify.

212. False conclusions a result of neglect of conditions. — A careful study of the literature of the subject reveals cases in which comparisons of nitrogenous substances have been made in which no potassic fertilizers whatever were employed, nor was evidence sought to

show that sufficient was already present in the soil to meet the maximum plant requirements. To this and to similar oversights may be attributed some part of certain of the discrepancies concerning especially the value of hoof meal and horn meal, although they may also have been due to the different methods of preparing the materials used by the different experimenters; and to the occasional unrecognized adulteration with substances of highly inferior character.

213. Results by Eckenbrecher. — A study of the efficiency of certain organic substances was made by Eckenbrecher, for a single season, in " sterile " sand from which, based upon nitrate of soda at 100, he classified the efficiency of the nitrogen in certain substances as follows: —

	For the Production of Straw	For the Production of Grain
Bone meal	100	77
Horn meal	91	56
Dried blood	86	65
Crude guano	6	6

It is evident that very different results might have been secured in normal soil.

214. Results by Kellner. — It was found by Kellner, in the warm climate of certain parts of Japan, that organic nitrogen was superior to nitrogen in sulfate of ammonia, due, presumably, to the rapid nitrification of the former, and to its loss by drainage before the plants could utilize it.

215. Results by Petermann. — Many experiments on the availability of organic nitrogen were made by A. Petermann in Belgium from which he concluded that nitrate

of soda should be given the highest rank. This was followed in efficiency by dried blood, then by wool which had been treated with sulfuric acid, next by bone meal, then by untreated wool, and finally by leather meal.

216. Precautions suggested by Wagner and Dorsch. — Extended studies of availability by Wagner and Dorsch [1] led them to lay down the following rules for such tests: (1) The experiments must cover several successive years. The same lots of soil must also be used throughout the whole period, and the same fertilization must be repeated annually. This is to aid in arriving at any cumulative effect of the organic fertilizers, in contrast to the supposed more temporary action of the nitrogen in nitrates. Concerning this recommendation, it may be said that its importance seems to have been somewhat overestimated in view of the many cases on record in which but relatively little effect is noticed, the second year, from heavy applications of organic nitrogen; furthermore, the cumulative effect of nitrate of soda in an acid soil, due to its basic properties and to the possibility of its nitrogen being partly transformed into "humous" combinations, may also be much greater than is sometimes recognized.

(2) The soil must contain sufficient lime to insure that there will be neither delay nor cessation of the process of nitrification.

(3) In selecting the soil, one should neither use one that is extremely favorable as concerns its physical character, nor one which is exceedingly poor, but rather a soil that would be ranked as medium in this respect. Later, if desired, the results may be studied under extreme conditions.

[1] Die Stickstoffdüngung der Landwirtschaftlichen Kulturpflanzen, Erster Theil, Berlin, 1892, pp. 242–258.

(4) One should introduce as many different organic nitrogenous fertilizers into the experiment as possible, in order that the results with a given substance may appear in their proper relation to those secured with other substances.

FIG. 8. — BARLEY, "UNLIMED."

1. No nitrogen. 2. Ammonium sulfate. 3. Leather. 4. Dried blood. 5. Nitrate of soda. Same amounts of potash, phosphoric acid, and nitrogen used in each case. Same as Fig. 9, except for the omission of lime.

(5) None of the fertilizers should be applied until spring, in order to avoid possible loss during the winter.

(6) In case a substance contains some other fertilizer ingredients than nitrogen, care must be taken, by the addition of an assured excess of all of them, to eliminate the possibility of their having influenced the result.

(7) All of the lots of soil must receive even slightly more of all the necessary fertilizers, other than nitrogen, than are necessary to the production of a maximum crop.

(8) Less nitrogen should be used in all cases than is necessary to the production of a maximum crop, in order that the best forms may exert their full effect.

(9) In order to make sure that the conditions under (7) and (8) have been surely met, nitrogen must be applied in at least two different amounts.

1 2 3 4 5 6

FIG. 9. — BARLEY, "LIMED" (EXCEPT 1).

1. No nitrogen, no lime. 2. No nitrogen. 3. Ammonium sulfate. 4. Leather. 5. Dried blood. 6. Nitrate of soda. All received like amounts of potash, phosphoric acid, and nitrogen. Like Fig. 8, excepting that lime was used for all but No. 1.

(10) The nitrogen content of the soil which is selected should be so low that fairly large applications of nitrogen may be made, for the accuracy of the results will be increased thereby.

(11) One should use relatively larger amounts of the less available substances than of the more active ones, in order that the experimental error may be made as nearly alike in all cases as possible.

(12) The experiments should be conducted on land

in its natural condition, as well as in pots; since the former provides against any possible errors due to higher temperatures in the pots, and the use of the latter insures against losses by drainage.

217. Results of tests by Wagner and Dorsch. — The experiments by Wagner and Dorsch were conducted with due recognition of the foregoing precautions, including tests in pots and in soil in its natural location. These experimenters call attention to the variation in the chemical and physical character of such nitrogenous materials from time to time; also to the wide variations in soil temperature, moisture content, and other factors that may modify results. Finally, as representative average figures expressive of the efficiency of the nitrogen in various materials, based upon nitrate of soda at 100, they give the following: —

	Relative Value
Nitrogen in nitrate of soda	100
Nitrogen in sulfate of ammonia	90
Nitrogen in dried blood, horn meal, and green (not yet woody) plant substance	70
Nitrogen in fine ground bone meal, meat meal (azotin), and dry ground fish	60
Nitrogen in stable manure	45
Nitrogen in wool waste	30
Nitrogen in leather meal	20

218. Results by Wheeler and Hartwell. — In experiments by Wheeler and Hartwell made in "Miami" silt loam, in deep pots set in the ground so as to make the interior and exterior soil level, sulfate of ammonia was found to be highly toxic, if employed without lime, but when used with lime its efficiency rose to 92 on the basis of 100 for the nitrogen in nitrate of soda. Similarly, on the unlimed soil the efficiency of the nitrogen in dried blood was but 45.5 on the same basis, whereas after liming

it was 90.3. Steamed, ground leather had an efficiency on the unlimed soil of but 0.9; but after liming the efficiency rose to 13.8, or to essentially the same figure noted by Wagner in many of his individual experiments.

219. Results by Voorhees. — In a series of experiments by Voorhees at the New Jersey experiment station it was found that the nitrogen of nitrate of soda was more available than that in any other materials. It was also found, when nitrate of soda was employed, that the crop was able to secure even a larger proportion of the soluble nitrogen derived from the soil and from the manures which had been added to it, than when no nitrate was used. Placing the value of the nitrogen in nitrate of soda at 100, the following seasonal variations in the efficiency of the nitrogen in other substances were observed by Voorhees: the value of the sulfate of ammonia was 99.5 in the year 1898, 77.9 in 1899, and 87.8 in 1900. The corresponding values found for dried blood in the three years were, respectively, 95.4, 61.3, and 73.1.

It was also shown by Voorhees that the soluble nitrogen in liquid manure possesses a high value. The insoluble nitrogen in fresh and leached barn-yard manures was found to become gradually soluble; and its value was much greater as the length of the period of growth was increased.

Views of Lawes. — In the climate of England, Lawes considered the nitrogen of shoddy and of most other organic substances as being only from one-half to two-thirds as efficient as that in nitrate of soda, sulfate of ammonia, and guano.

220. Results by Kellner on wet soil. — It has been shown by Kellner that in the wet rice fields of Japan ammonia, instead of nitrates, is formed from organic nitrog-

enous substances. In his experiments with rice he used in one series twice as much nitrogen as in the other, and in both cases liberal quantities of phosphoric acid and potash. The applications were also made some days in advance of the setting of the rice plants in order to avoid toxic effects from a too rapid formation of ammonia at the outset. The natural soil, when air-dried, contained 0.61 per cent of nitrogen. Under such circumstances, in the warm climate which prevailed, the relative efficiency of the various materials, based upon the mean of the gain in crop, and of the nitrogen recovered, was found to be as follows: —

	Relative Efficiency
No manure	0
Sulfate of ammonia	100
Bone meal, steamed	142
Fish-scrap, 9.9 per cent of nitrogen	135
Fish-scrap, 9.5 per cent of nitrogen	133
Blood meal	130
Bone meal, raw	120
Distillery slop, dried	118
Horn meal	116
Peruvian guano	116
Press cake	104
Rape cake	106
Night soil	106
Farm manure	88
Rice husks	48
Green plants	42

Owing to the fact that irrigation waters were used on the lands where the foregoing tests were made, the materials containing nitrogen which was wholly or partly soluble were at a great disadvantage, as compared with the materials from which the nitrogen could not be so readily dissolved and carried away. This applies particularly to the sulfate of ammonia, farm-yard manure, night soil, guano, and materials of similar character. It is obvious, therefore, that the figures in the preceding table are ap-

plicable only to similar conditions and not to those usually existent on farm lands.

221. Results by Seyffert. — In experiments by Seyffert with kohl-rabi, in which identical amounts of nitrogen were used in all cases, in the various materials, the following results were secured: —

	Grams of Crop
No nitrogenous fertilizer	76
Crude Mejillones guano	71
Leather meal, steamed	469
Steamed bone meal	1572
Dried blood	1654
Horn meal, steamed	2005
Nitrate of soda	2608

222. Results by Heinrich. — Experiments are on record by Heinrich in which he found, with oats, that there was no material difference in the efficiency of the nitrogen in leather meal and in blood meal. This result is, however, so completely out of accord with the experience of other experimenters that serious doubt is cast upon the genuineness of the blood meal, or upon the suitableness of the conditions under which the experiment was conducted, or possibly upon the interpretation of the experimental data.

223. Results by Johnson. — According to S. W. Johnson's experiments with Indian corn, certain organic nitrogenous fertilizers should be rated in efficiency as follows: —

Nitrate of soda	100
Castor pomace (best results)	85
Linseed meal	80
Dried blood	77
Cotton-seed meal	76
Castor pomace (poorest results)	74
Hoof and horn meal	72
Dried fish	70
Tankage	68

224. Results by the nitrification method of Müntz and Girard. — Experiments were made by A. Müntz and Girard to determine the relative value of nitrogenous fertilizers by subjecting them to nitrification and measuring the amount of nitrates produced at the end of 30 and 39 days. This resulted in showing that the nitrogen in sulfate of ammonia should be ranked ahead of that in organic compounds. This was followed in order by the nitrogen of guano, bat manure, leguminous plants used as green manure, dried blood, meat meal, horn meal, and roasted horn. Roasted leather was found to nitrify very slowly, and raw leather not to any practical extent.

225. The pepsin method. — Many investigators in the United States and in Europe have studied the solvent action of pepsin solution upon various organic nitrogenous substances as a means of determining their crop-producing value. The results in many cases accord fairly well with those secured in tests with plants, though certain gross disagreements have been noted. It was found in the course of this work that a preliminary treatment of the material with borax increased the solvent action of the pepsin.

226. The permanganate method. — In the hope of finding some more reliable chemical method than that afforded by treatment with pepsin, many experiments with potassium permanganate have been made in acid, neutral, and alkaline solutions. Recently the agricultural experiment stations of New England, New York, and New Jersey have adopted, tentatively, the treatment with an alkaline solution of potassium permanganate, for the purpose of furnishing evidence as to the probable efficiency of the insoluble organic nitrogen in ready-mixed commercial fertilizers. The organic residues, remaining after extract-

ing the fertilizers with water, are being tested, by way of pot experiments with plants, in order to ascertain how far this chemical method of treatment is in accord with the degree of availability shown by plants in normal soil.

227. Lipman's ammonification method. — Recently Lipman [1] and others have suggested the determination of the availability of organic nitrogen by the rate at which ammonification occurs, under definite conditions. According to Lipman, the results by this method agree sufficiently well with those secured in vegetation experiments with plants, to justify its employment in many cases. Attention is called to the fact that the rate of ammonification is affected by the carbohydrate content of the soil and by other factors.

[1] Centralb. f. Bakt., *31* (1911), 49–85.

CHAPTER XII

CALCIUM AND POTASSIUM NITRATES

Calcium nitrate and potassium nitrate are two especially useful sources of nitrogen which will be considered in detail.

228. Calcium nitrate a new fertilizer. — Calcium nitrate is a comparatively new product in so far as concerns its production and use for agricultural purposes, and it is but just being introduced into this country in an experimental way, though it has been used to some extent in Europe for a very short time. This nitrate has been long and favorably known as one of the important compounds formed in soils in connection with the usual processes of nitrification.

229. Production possible due to cheap electricity. — Recently, due to the great developments in the line of cheapening the cost of electricity, it has become possible, by employing an electric arc furnace, to oxidize the nitrogen of the air to nitrous oxid and nitric oxid. In fact, in 1898 Sir William Crookes predicted that the world's supply of nitrogen would soon come from the air. He pointed out that all that was needed was some means of maintaining the energy necessary to cause the continuous union of oxygen and nitrogen on a sufficiently large scale. Based upon the work of Lord Raleigh, he further expressed the belief that with the perfection of the electrical plant at Niagara Falls this would be accomplished.

230. The work of Lovejoy and Bradley. — Soon thereafter Lovejoy and Bradley, by producing several arcs between platinum poles with a continuous current of 10,000 volts, generated oxid of nitrogen which was converted into a mixture of sodium nitrite and sodium nitrate. This process proved, however, too destructive to the apparatus to be remunerative.

231. The process of Birkeland and Eyde. — The later process developed successfully by Birkeland and Eyde involves the use of an alternating current of not more than about 5000 volts. An arc is formed between U-shaped copper electrodes cooled from within by a current of water. The arrangement of the two hollow electrodes is such as to produce a flat and broad flame, the temperature of which, though only 2600° C., is not so luminous as might be expected. The flaming electrical arc is moved backward and forward by a magnet in such a way as to produce a maximum of contact and consequent oxidation. About 2694 cubic feet of air are passed through the furnace, per minute, where it is subjected to an alternating current of from 3000 to 4000 volts, giving a flame 6 feet in diameter. When the air emerges, its temperature is from 600° to 700° C. It then carries about 1 per cent of nitric oxid and is next passed through a steam boiler in order that it may give up a part of its heat, in the generation of steam. The current is then passed through two oxidizing chambers. Here it takes on oxygen from the air, after which it is passed through five condensing towers, each of which is about 50 feet high. In the meantime, water is allowed to trickle down the broken quartz with which four of the towers are filled; and by the time it has reached the bottom of the fourth, it contains approximately 5 per cent of nitric acid. This solution is then passed

down the third, second, and first towers successively, and, upon reaching the bottom of the last of these, it contains 50 per cent of nitric acid. From here it passes to a fifth tower, which contains milk of lime, and, finally, to a sixth tower, which carries beds of lime. In this last tower the solution is absorbed, and there is formed a mixture of calcium nitrite and of calcium nitrate. This product upon treatment with some of the nitric acid is all changed into nitrate, and the nitrous fumes which result are led back to the oxidizing chamber. The final product, after concentration, is poured, in a molten condition, into canisters for shipment.

232. First product too hygroscopic. — The crystallized nitrate of lime which was produced at first was so hygroscopic that it would melt if held in the hand, and it became necessary to mix it with peat dust before its application to the soil.

233. Processes for lessening hygroscopic tendency. — Later attempts have been made to make a basic nitrate of lime, but this contained only 11.7 per cent of nitrogen, and hence increased to a serious extent the cost of transportation per unit of nitrogen. Subsequently a partially dehydrated salt was produced containing 13 per cent of nitrogen.

In order to obviate the tendency of nitrate of lime to deliquesce, it has been mixed at times with alkaline sulfates, with sulfate of potash, sulfate of magnesia, and with calcined kieserite. By such treatment a powder is formed which is said to afford no more difficulty, in this particular respect, than is met with in the handling of nitrate of soda.

234. Chemical composition. — The solidified or powdered product of calcium nitrate contains about 25 per cent of lime in an unchanged condition. It also contains 13

per cent of nitrogen, which is equivalent to 75 per cent of calcium nitrate.

235. Calcium nitrate as a fertilizer. — The chief drawback to the practical use of calcium nitrate as a fertilizer has been its tendency to deliquesce readily, especially in a moist climate.

Since calcium nitrate carries an excess of lime, it is an ideal source of nitrogen for certain of the granitic, gneissic, slate, shale, and sandstone soils, many of which are often practically devoid of carbonate of lime; but on calcareous soils, and for plants that do not respond favorably to liming, it may be much less valuable. The tendency of calcium nitrate is the direct opposite of that of sulfate of ammonia, for the latter rapidly exhausts the calcium carbonate supply of the soil. In actual practice the results secured with calcium nitrate appear to lack more or less in agreement. This is doubtless due to the fact that sufficient attention has not always been paid to the quite different character of the soils under experiment, and to the widely varying effect of lime upon the growth of the different varieties of plants, for which it has been used. In general, however, the results from the use of calcium nitrate have been highly favorable, agreeing well with those secured with nitrate of soda.

236. Danger of the earlier products injuring horses and workmen. — Attempts to sow calcium nitrate broadcast by itself are said to be likely to result in serious injury to the hands and eyes of the workmen. If one attempts to use a machine, such as is ordinarily employed for distributing fertilizers, it flows too freely to admit of its uniform and satisfactory distribution. On this account it has been suggested that the material be mixed with soil or with some other suitable dry substances before its dis-

tribution. It has been used mixed with calcium cyanamid with better results than when the cyanamid is used alone.

237. Extent of the output of calcium nitrate. — In the first three months of 1908 the output of the Norwegian Hydro-electric Nitrogen Works of Christiana was 1059 tons of calcium nitrate; or more than in the entire previous year. Since that time other plants have also begun operations. In April, 1911, it was reported that the total available output until August of that year was already sold; and that, with the completion of the new works then under construction, it was expected that the annual production would reach 100,000 tons.

238. Cost of producing calcium nitrate. — The present price of calcium nitrate is based upon that of nitrogen in nitrate of soda, on which basis it can be produced at a good profit. In fact, it has been claimed that with the present cheap electric current, generated in Norway, calcium nitrate can be manufactured at a price 30 per cent cheaper, per unit of nitrogen, than the present ruling price of nitrogen in nitrate of soda.

239. Other processes. — Other modified processes for the manufacture of calcium nitrate have been devised by E. Rossi, in Italy, and by G. Erlwein, who is in the employ of the firm of Siemens & Halske, in Germany.

240. Sources of potassium nitrate. — Impure potassium nitrate, known commercially as "niter" or "saltpeter," is found naturally in certain parts of India, also near Mabelstadt and Peliska in Cape Colony, South Africa, and in other countries, where it appears as a white incrustation on the surface of the soil. It is also often found mixed with the soil to a considerable depth.

The nitrate is extracted from the earthy matter by water. The solution is then evaporated by exposure to

the rays of the sun, or by artificial heating, after which it is allowed to stand and crystallize. In this crude or partially purified condition it is known as "grough," and it usually contains about 44 per cent of potassium oxid and 11 per cent of nitrogen. There is frequently associated with the potassium nitrate from 1 to 10 per cent of impurities, chief among which are sodium chlorid and sulfates of soda, potash, and lime.

241. Artificial niter beds. — Potassium nitrate has also been prepared at times in artificial niter heaps or beds. Such heaps are prepared under a shelter, where there is an impervious floor to prevent the escape of liquids. The side of the heap most exposed to evaporation is often kept vertical, whereas the other side is built up in the shape of successive grooved terraces upon which the drainage from stables is occasionally conducted. In this way the fermentation of the vegetable and animal matter, which is mixed with limestone, old mortar, wood-ashes, or similar basic material, is readily promoted. The nitrates which are formed are finally leached to the vertical side of the heap, where they accumulate as an efflorescence, due to the continual evaporation at that point. When the accumulation has become great enough to justify it, the outside vertical layer and the nitrate accumulated on its face are removed. The material is next extracted with water and is still further purified by crystallization. The residual matter, after its extraction, is returned to the terraces on the rear of the heap. Usually the heaps are torn up and rebuilt after from two to three years.

A temperature of from 60° to 70° F. is considered favorable to the nitrifying processes, though, as is well known, the optimum temperature for nitrification is probably about 98° F.

There was long much mystery about the cause and the nature of the changes actually taking place in such beds, but this has been removed by the work of Frankland, Warrington, Winogradsky, and others, who have shown that the changes are the result of the activity of certain species of microörganisms.

The chief nitrates associated with the potassium nitrate from such artificial beds are nitrates of lime, magnesia, and ammonia. These may all be converted into potassium nitrate, however, by treatment with potassium carbonate.

242. Made for industrial purposes from nitrate of soda. — For industrial purposes, potassium nitrate is manufactured from the Chilian nitrate of soda and potassium chlorid.

243. Potassium nitrate often economical for agricultural use. — It is usually asserted that, potassium nitrate, on account of its high price, finds little or no application in agriculture, excepting in a small way in certain special garden fertilizers, and that the elements which it furnishes can be secured more cheaply in nitrate of soda and in muriate of potash. Nevertheless, it has often happened in recent years in the United States that niter has been the most economical source of potash and nitrogen on the Atlantic seaboard, and at points where the transportation charges on fertilizers are still greater, it may frequently be found economical for agricultural uses.

244. Chlorin avoided by using potassium nitrate. — Potassium nitrate is especially applicable wherever large amounts of chlorin are objectionable; as, for example, for tobacco, sugar beets, and for certain other field crops, but more particularly in greenhouses, where toxic residues should be especially avoided.

CHAPTER XIII

NITRATE OF SODA

The most widely used and known of all nitrate fertilizers is nitrate of soda, which, owing to its vast agricultural importance, will be discussed in its various relationships to plants and soils.

245. Sources of nitrate of soda. — Quantities of nitrate of soda of economic importance occur in Egypt, and minor deposits also in the pampas of Peru, Chili, and Bolivia. The chief deposits in the world are found in the plateau of Tarapaca in northern Chili (formerly Peruvian territory), and in the desert of Atacama. This plateau, which is merely an elevated sea bed, is now from three to four thousand feet above the level of the ocean. It extends for approximately seventy-five miles north and south, and from twenty to twenty-five miles from east to west. The plateau where the nitrate is most abundant is shut in by the Cordilleras on the east and by a low range of foothills on the west. Rain seldom falls there more frequently than every two to three years, and then in such small quantities that it evaporates quickly. Immediately on the surface of this plateau is found a rock known as "costra," carrying occasionally small amounts of phosphates, but consisting chiefly of sand and gypsum. Beneath this lies the "congels," a conglomerate rock composed of gravel and clay. Underneath the whole lies the "caliche" or impure nitrate of soda associated with earthy matter and

with salts of calcium, magnesium, and potassium. The overlying rocks range usually from three to ten feet or more in depth, while the caliche may vary in depth from a few inches to from 8 to 10 feet. Its average depth is about 3 feet.

246. Concerning the origin of the Chilian nitrate of soda. — Several theories have been advanced to explain the mode of origin of the nitrate. (1) It has been suggested that the nitrates have resulted from natural electrical discharges by which the nitrogen of the air has been fixed, resulting in the final formation of nitrates. The suggestion has also been made that the carbonates of the alkalies and of the alkaline earths have aided in the oxidation of the atmospheric nitrogen.

(2) That the nitrate was formed from guano deposits, which upon nitrification yielded calcium nitrate. The calcium nitrate is believed to have then reacted with sodium chlorid and with other sodium salts of some inland salt lake by a process of change analogous to one said to be taking place at the present time in Hungary. By the reactions suggested, sodium nitrate is supposed to have been produced. The resulting calcium chlorid is believed to have been largely removed in solution. This view of the origin of the beds is supported also in some measure by the presence of sodium chlorid in the caliche. The lack of considerable amounts of phosphate, associated with the deposit, is, however, considered as an objection to this theory.

(3) That in the elevation of the plain from the bed of the ocean great numbers of marine animals and vast quantities of the great sea-weeds, which are common on the Pacific coast of North and South America, were raised to a position where their decomposition and ultimate nitri-

fication took place readily. The small amounts of phosphates in the overlying rocks have been considered as supporting evidence of this origin, and likewise also the presence of iodates in the caliche. It is inconceivable, however, that the volume of sea-weed could have been sufficient to supply all of the vast quantity of nitrogen; and, furthermore, the absence of bromin, which is a constituent of sea-weeds, is a serious blow to this theory.

(4) It is more probable for many reasons that the nitrates had their origin in the higher mountain ranges, perhaps chiefly at a much earlier time when the rainfall was more abundant, and that the evaporation of these saline waters, due to progressive desiccation, gave rise to the present deposits. It remains, however, to be explained by this theory, from what source the iodin was derived. This idea of the origin of the nitrates is upheld by A. D. Hall, whereas another recent English writer adheres to the idea of their having been formed from sea-weeds.

Recent investigations by Headden and Sackett [1] as to the cause of the excessive accumulations of nitrates, which are found to be highly destructive to apple orchards and to some farm crops in certain sections of Colorado, have shown that nitrogen is fixed from the air in great quantities, chiefly by *Azotobacter chroococcum*. The extent of fixation in a sample of soil from the Colorado college farm, in the course of a period of incubation extending over 27 days, is said to have been equal to 5222 pounds of nitrogen, or to 17.5 tons of "proteids" per acre-foot of soil, per annum. If the rate of increase of nitrate nitrogen observed by Headden, for a period of 48 days, were main-

[1] Buls. 178 and 179, respectively, Agr. Expt. Sta., Colorado Agricultural College.

tained continuously for a year, it would amount to four and one-third tons of nitrates per acre-foot of soil. In a later article [1] Headden states that " The area in which the nitrogen fixation by the *Azotobacter* is actually taking place in Colorado under our semi-arid conditions is sufficiently extensive to entitle the suggestion, that the nitrogen present in the Chili-saltpeter was also fixed by *Azotobacter*, to serious consideration." Hilgard also calls attention to the great quantities of nitrates in certain of the soils of California; and in one locality, over an area of ten acres, they were found at the rate of 1200 pounds per acre, the maximum being two tons per acre.

(5) It has been pointed out recently by Kuntze that the vicuñas and llamas are now known to have roamed in immense numbers, probably since time immemorial, over that part of the Andes where the nitrate deposits occur, and the fact that they always deposit their dung in the same place points to such accumulations as a possible source of the nitrates. The common salt is accounted for, according to this theory, as coming from the urine and excrement, and from the alkaline salts resulting from rock decomposition. This theory does not, however, account for the iodin which has long been one of the chief supports of the sea-weed theory of the origin of the nitrate.

It appears quite possible that two or three of these different sources may have contributed to the deposits.

247. The first exploitation of the nitrate of soda. — Notwithstanding that the existence of the nitrate fields had been known since a much earlier date, the first shipments of nitrate of soda were not made from Iquique until 1830. These amounted to 800 tons. In the next ten years the annual output had risen to 10,000 tons, and

[1] Proceedings of the Colorado Scientific Society, *10* (1911), 120.

in 1907 it amounted to 1,660,000 tons, and it has since been rapidly increasing.

248. Chemical composition and purification of the nitrate of soda. — The crude caliche contains only from 17 to 60 per cent of nitrate of soda. The native material is removed from its beds by the use of dynamite. It is then freed from the associated earthy matter by dissolving in hot water, after which it is allowed to crystallize out in tanks. The crystals are then removed, dried, and bagged ready for shipment. The mother liquors are subsequently utilized for the recovery of iodin compounds and certain other valuable salts. In its commercial state, nitrate of soda contains from 95 to 97 per cent of nitrate, or from 15 to 16 per cent of nitrogen, which is equivalent to 18 to 19 per cent of ammonia. Pure nitrate of soda contains 16.47 per cent of nitrogen, equivalent to 20 per cent of ammonia, but this is too costly for agricultural uses.

249. Impurities in nitrate of soda. — The impurities present in the commercial nitrate of soda employed for agricultural purposes are 2 to 3 per cent of water, 0.5 to 1.5 per cent of sodium chlorid, small amounts of sodium sulfate, potassium sulfate, and calcium sulfate; also sodium iodate and traces of other less important salts. Sometimes even potassium nitrate may occur as an impurity in nitrate of soda, though it is usually very largely removed in the mother liquors. The only impurity that is troublesome agriculturally is sodium perchlorate, which has sometimes been found in quantities equal to from 6 to 7 per cent. Amounts in excess of 1 per cent have been found to be harmful to crops, causing, in the case of cereals, a peculiar twisting of the leaves and poor development of the stalk which does not occur under normal conditions. In recent years, due doubtless to greater precautions in the

course of the purification, few, if any, complaints of injury due to the presence of perchlorate have been heard.

It is only in the rarest instances that adulteration of nitrate of soda has been met with, a fact doubtless due to vigilant inspection, and to the ease with which foreign materials can be recognized by chemical and other means.

250. Physical characteristics of nitrate of soda. — The color of the commercial nitrate of soda ranges from brown and pink to grayish white. It becomes lumpy as a result of storage, and for this reason it is often reground when sold for the home-mixing of fertilizers. It is important to store nitrate of soda in a reasonably dry location, or it will readily liquefy to some extent by the absorption of water from the air.

251. The availability of nitrate of soda as plant food. — Nitrate of soda ranks with potassium nitrate and calcium nitrate as one of the most efficient of all nitrogenous fertilizers, for it can be utilized by plants at once without the necessity of undergoing preparatory fermentative changes.

252. Quantities to apply and care in using. — Nitrate of soda is applied in quantities ranging usually from 100 to 400 pounds per acre, though as high as 600 to 800 pounds are sometimes employed for special purposes.

Great care must be taken, in top-dressing spring grains, grass fields, and lawns, to apply the nitrate of soda when the grass is dry, for otherwise the tips of the leaves may be severely burned. Bags of the material should not be left standing on moist lawns or meadows, or the grass underneath will be likely to be killed. Owing to its destructive power, particular attention must be paid to keeping nitrate of soda away from immediate contact with the seed.

In connection with spring top-dressing, it is important

No nitrogen | 21 lb. nitrogen per acre | 63 lb. nitrogen per acre

FIG. 10. — GRASS, SEVERAL YEARS AFTER SEEDING.

All fertilized alike with lime, potash, and phosphoric acid. Timothy most abundant where much nitrate of soda was used.

to bear in mind that if nitrate of soda is applied early, it tends to promote tillering and hence increases the number of stalks of grass and of cereals, sometimes, in the latter case, even at the expense of the yield of grain. If, on the contrary, the application is delayed until the tillering is complete, it merely aids in the development of the stalks already in existence. It is usually desirable to top-dress grass at an early date in the spring, not only to promote tillering, but also in order to push the growth as much as possible while abundant water is still present in the soil.

253. Nitrate of soda corrects soil acidity. — It is a well-established fact that the use of nitrate of soda may gradually improve the condition of certain acid soils which are naturally deficient in carbonate of lime, whereas sulfate of ammonia may render their condition far worse. This fact was strikingly demonstrated at the Rhode Island experiment station in the years from 1891 to 1900. Later also a similar result followed the use of a mixture of ammonium sulfate and ammonium chlorid, by Voelcker, at Woburn, England. In fact, in 1881 Adolf Mayer,[1] in classifying various agricultural chemicals, referred to nitrate of soda as being "physiologically basic." This was on account of the fact that the acid is utilized by plants to a greater extent than the sodium, in consequence of which the latter is transformed, in the soil, into sodium carbonate.

254. Physical effects of the residue from nitrate of soda. — The residual sodium carbonate from nitrate of soda may result injuriously or beneficially, according to the character of the soil. It is well known, for example, that on heavy clay soils, especially if deficient in vegetable matter, the continued employment of nitrate of soda may

[1] Landw. Vers.-Sta., *26*, 94, 95.

give rise to so much sodium carbonate as to seriously deflocculate the clay, by which its tendency to bake is enormously increased. The ability of such soils to admit air, and to absorb and deliver water to the plant in proper amounts, is also greatly impaired thereby. In such cases liming has not always been found to be an effective remedy, and it has been recommended to use acidic fertilizers, such as acid phosphate, sulfate of ammonia, and muriate of potash, which are said to correct the condition satisfactorily.

255. The residual soda may liberate potash. — Attention has been called by Hall and others to the action of the soda of the nitrate of soda as a liberator of potash in soils, whereby the arising of potash deficiencies may be delayed for several seasons.

256. Residual soda can replace potash in part. — Several years ago, also, Paul Wagner in Germany and Atterberg in Sweden called attention to the fact that soda could probably replace potash to a certain extent, in which case it might be expected to act as a conserver of the potash supply in the soil. This idea is also supported by experiments at the Rhode Island agricultural experiment station. In one instance sodium carbonate, as well as sodium chlorid, more than doubled a crop of mangel wurzels when as much as 330 pounds per acre of muriate of potash, or its equivalent of potassium carbonate, had been added in the fertilizer. In the case of certain other crops which do not take up large amounts of soda under any circumstances, the benefit from using extra sodium salts was small, and yet further applications of potassium salts were beneficial. It was evident, therefore, that the soda in some cases had been chiefly helpful in some other way than as a liberator of potash.

The idea that soda is able to perform certain functions, or at least a part of certain functions, in plants, which would be performed by potash if a sufficient supply of the latter were available, was also observed at the same station. This was shown by water-culture experiments in which the possibility of indirect manurial action, through the liberation of potash, was not only eliminated, but also any effect of increased osmotic pressure, and of other factors which might possibly exert an influence upon plant growth.

257. The soda of nitrate of soda may in certain cases conserve the soil potash. — Many analytical data secured in Rhode Island with field crops, grown by the use of varying amounts of sodium and potassium salts, showed that at least certain of the " root " crops may take up far more soda and potash than seem strictly essential to bring about a given crop yield. If soda is absent, this overloading of the plant with alkali is at the expense of the potash supply of the soil. If soda is used in the fertilizers, this " hunger " for alkali is partially satisfied with soda, and the potash supply of the soil is consequently conserved for future crops. It seems probable that some writers have paid too little attention to this feature. They have consequently attributed the indirect effect of the nitrate of soda too largely to liberation of potash from zeolitic combinations in the soil.

258. Soil improvement by using nitrate of soda. — A striking instance of soil improvement as a result of the use of nitrate of soda is afforded at the Rhode Island experiment station, where it has been used continuously from 1893 to 1912. At the outset the soil was so deficient in carbonate of lime that only an occasional clover plant could withstand the existing conditions. The lack of

available basic substanees was in faet so great that a single moderate applieation of sulfate of ammonia, on a neighboring plot of land, proved immediately toxic. Notwithstanding this, by the long-eontinued use of nitrate of soda, even without the aid of lime, the produetiveness of the soil for most agrieultural plants has shown marked improvement, and the successful eultivation of elover on the land has been rendered more nearly possible. In faet, the present conditions are but little, if at all, inferior, for most varieties of plants, to those where sulfate of ammonia has replaced the annual applieations of nitrate of soda and where several heavy applications of lime have been made in the period of nineteen years. It is evident, therefore, that nitrate of soda has a decided basie effeet; and on an aeid soil, of a physieal eharaeter not readily injured by defloeeulation, it may readily bring about long-enduring and marked improvement in erops.

259. Nitrate of soda may injure certain soils. — It must be obvious that in arid or semi-arid regions where the soil is suffieiently basie, or is already unduly so, nitrate of soda, if used eontinuously, might soon magnify the eondition to a limit of danger, espeeially to all of those erops whieh are highly sensitive to basic eonditions.

From what has preeeded it is evident that no general rule for the use of nitrate of soda ean be formulated whieh is applieable to all classes of soils, for one must take into aeeount their physical and ehemieal eharaeter as well as the peculiar adaptations of the individual plants to be grown.

260. Benefit not due solely to hygroscopic effects. — It appears probable that mueh of the benefit from the use of nitrate of soda, whieh was formerly attributed to its increasing the hygroseopic eharaeter of the soil, may

have been due to certain of the beneficial effects which have just been discussed, but which were formerly unrecognized or but little understood.

261. The soda as a carrier of phosphoric acid into plants. — It has been found at the Rhode Island experiment station that the use of common salt or sodium carbonate in fertilizers tends to an increase in the phosphorus content of certain root crops; and since sodium carbonate is formed in the soil in consequence of the employment of nitrate of soda, the use of the nitrate must eventually result in the same effect. Such benefit is, however, not confined to root crops, for in experiments with cereals Wagner and Dorsch [1] find support for the experiments by Emmerling, Loges, Beseler, and Maercker, to the effect that by the use of nitrate of soda there resulted a larger yield, with more economical utilization of both phosphoric acid and potash, than when nitrate was not employed.

262. Nitrate of soda conserves the lime supply of the soil. — In the examination of drainage waters at the Rothamsted experiment station it was found, in the case of some of the plots in Broadbalk field, that the application of nitrate of soda had lessened the annual loss of carbonate of lime by from 200 to 300 pounds per annum.

263. Nitrate of soda not a stimulant. — Nitrate of soda is often referred to as a plant stimulant, or, in other words, according to the definition of one of the leading authorities, as something "Producing increased vital action in the organism at any of its parts." The term "stimulant" should, however, preferably be applied to that which acts in the manner described, but which does not enter into and form an essential part of the organism itself, and which is normally foreign to it. It is obvious that

[1] Die Stickstoffdüngung der Landw. Kulturpflanzen, Berlin, 1892.

nitrate of soda is not a stimulant in this latter sense, and that all of the elements absolutely essential to plant growth might with equal propriety be called stimulants. For example, a plant reared in a medium free from iron soon becomes chlorotic, but recovers almost immediately upon its application to the nutrient medium. In fact, the recovery is essentially as quick as that of plants when supplied with nitrates, in cases where available nitrogen is greatly needed. It is indeed a misfortune, because of the quick action of certain fertilizers, that the term "stimulant" should ever have been applied to them, for they actually yield to the plant essential elements of plant food. As concerns the public, the designation of certain plant food ingredients as stimulants tends to create an unwarranted prejudice against them, and the farmer is falsely led to believe that, following their first beneficial effect, conditions unfavorable to his crop are likely to arise.

Much of the former prejudice against nitrates, on the ground that they are stimulants, has doubtless arisen from observing the frequent temporary benefit from their use when unaccompanied by the other ingredients of plant food. It ought to be plainly evident, however, if a soil is but sparingly provided with available potash and phosphoric acid, that liberal applications of nitrates will cause these other soil ingredients to become exhausted much sooner than otherwise. In such cases the nitrates have not acted as stimulants, but have merely furnished the missing ingredient required in the manufacture by the plant of the readily available potash and phosphoric acid of the soil, into the finished crop product. It must be obvious that these materials cannot be utilized in the building of plants and still remain in the soil for the benefit of crops which follow.

264. Nitrate of soda yields quick returns on the manurial investment. — The old idea that the more the effect of a fertilizer can be prolonged in the soil, the more economical it is, must give way to the idea that the quicker the returns on the money invested in the fertilizers, the greater are likely to be the net profits. It is, however, important to recognize that there may sometimes be cases in which a given investment in a large quantity of a very cheap, slowly acting fertilizer may be more remunerative than the purchase for the same sum of money of a small amount of one which acts quickly. In such cases the price per ton, the amount of plant food contained therein, the danger of loss or of unfavorable transformations resulting in the soil, and the length of time before it will be possible for the plants to make use of it, must all be given due consideration. When so considered, nitrate of soda will not be looked upon as a " stimulant " or as something to be avoided, but as an excellent fertilizer. Nevertheless, nitrate of soda is a fertilizer which must be used with good judgment. One must consider not only the length of the period of growth of the plants concerned, but also their special characteristics and requirements. Attention must also be paid to the character of the soil as concerns the possibilities of loss by drainage; and to the effect of the nitrate of soda upon the soil texture and its chemical reaction.

265. Possible effects of nitrate of soda on the microorganisms of the soil. — To what has preceded may be added the possible consideration of the effect of the nitrates upon the microscopic plant and animal life of the soil, since a disturbance of the numerical relation of certain of these two forms and even of the different microscopic plants (including bacteria) may have a marked influence upon the productivity of the soil.

266. Ammonium nitrate. — At present ammonium nitrate (NH_4NO_3) is rarely used for agricultural purposes because of its high cost; yet it is a most excellent fertilizer, especially where it is desirable to employ a source of nitrogen which will leave in the soil no objectionable residues. Such conditions are most frequently met with in greenhouses, where, owing to the great value of the product from a small area, its use may often be permissible. Ammonium nitrate contains 35 per cent of nitrogen, one part existing in ammoniacal and the other in nitrate form. This material possesses one very distinct advantage over all of the usual nitrogenous fertilizers, for the reason that the cost of transporting a unit of nitrogen is very low. This is on account of its concentrated character and the fact that it does not contain some occasionally useless or low-priced ingredient such as soda or lime.

267. The synthetic production of ammonia and ammonium salts. — Experiments are now being conducted which have shown the possibility of the synthetic production of ammonia by the compression of hydrogen and nitrogen at high temperatures in the presence of uranium oxid, pure iron, and of other catalyzers. If this process can be placed on an economic basis, as is claimed, the manufacture of ammonia and of nitric acid may yet be made so cheap that ammonium nitrate can be generally used as a fertilizer. An important feature of this process is that the union of the gases does not depend upon powerful electric currents. On this account great water power is not vital to success, and the manufacture can therefore be carried on practically anywhere.

CHAPTER XIV

AMMONIUM SALTS AND CALCIUM CYANAMID

The ammonium salt of the greater agricultural importance at present is ammonium sulfate. This is derived chiefly from the destructive distillation of coal in coke ovens, blast furnaces, gas works, and elsewhere.[1]

268. The manufacture of ammonium sulfate. — It is asserted that the first attempt to recover the ammonia in connection with the manufacture of coke was made by Stauf in 1764, but the first satisfactory plant for this purpose was not erected until 1858, when one was established at St. Denis.

The amount of nitrogen in coal ranges from 1.5 to 2 per cent, and of this only about 15 per cent is transformed into ammonia and recovered in the water used for washing the gas. The ammonia is redistilled from this water, collected in sulfuric acid, and the resulting sulfate of ammonia is won by crystallization. It yields a white, yellowish, or gray salt containing about 20.5 per cent of nitrogen. The appearance of the yellow, gray, or occasional blue or brown color may be due to traces of tarry products, ferrocyanid, formed from cyanids which are usually present, and to materials sometimes accompanying thiocyanates.

269. Thiocyanates a former toxic impurity of ammonium sulfate. — The presence of thiocyanates is readily

[1] For the details of this process, see The Manufacture of Chemical Manures, by Fritsch, London, 1911.

recognized by the reddish coloration produced when ferric chlorid is added to a watery solution of sulfate of ammonia. Its occurrence in quantities sufficient to be deadly to vegetation has been noted in sulfate of ammonia sold in Europe; but because it is so easily recognized, and the importance of its avoidance is now so well understood, it is seldom encountered. It was present a few years ago in a lot of sulfate of ammonia sold in Rhode Island, but the quantity was found by experiment insufficient to prove positively toxic to the usual farm crops.

270. Chemical composition of sulfate of ammonia. — When pure, sulfate of ammonia contains 21.2 per cent of nitrogen. The commercial product is usually sold under a guaranty of 20.2 per cent of nitrogen or 24.5 per cent of ammonia.

271. Sulfate of ammonia must not be mixed with alkaline substances. — Owing to the ease with which ammonia is liberated by alkalies, sulfate of ammonia should never be mixed, before its application, with wood-ashes, potassium carbonate, slaked or burned lime, basic slag meal, or other materials of similar basic character. Considerable losses have been said to result after the application of sulfate of ammonia to a rich garden soil that had been liberally limed. Similar losses also occur from light calcareous soils in times of drought. Ordinarily, however, there is but little loss of ammonia by volatilization when sulfate of ammonia is applied to soils as a fertilizer, under the usual conditions and in the usual amounts. Indeed, there is much evidence to this effect, even in the case of soils which have been adequately, though not excessively, limed.

272. Absorption of sulfate of ammonia by soils. — The ammonia of ammonium salts is usually readily ab-

sorbed by soils, in such a way that it is less subject than nitrates to immediate losses by leaching. This is probably due to the fact that the ammonia enters at once into chemical combinations with certain organic salts, formed by the reactions of lime and magnesia with products of decaying vegetable matter, and also with zeolites and possibly other similar compounds of the soil. The sulfuric acid of the sulfate of ammonia unites with the bases which are replaced by ammonia. The ammonia, in these combinations which result in the soil, nevertheless yields readily to nitrification.

273. The use of sulfate of ammonia exhausts soils of lime. — It was long supposed that most of the ammonia thus retained by soils was transformed at once and held as ammonium carbonate, the compound which results from the reaction of ammonium sulfate with calcium carbonate, as follows: —

$$\underset{\text{ammonium sulfate}}{(NH_4)_2SO_4} + \underset{\text{calcium carbonate}}{CaCO_3} = \underset{\text{ammonium carbonate}}{(NH_4)_2CO_3} + \underset{\text{calcium sulfate}}{CaSO_4 \cdot Aq.}$$

By this reaction calcium sulfate (land plaster or gypsum) is formed, which in time is largely lost by its solution and passage into the drainage waters, whereby the soils gradually become deficient in lime. Furthermore, by the later nitrification of that portion of the ammonia which is not changed to carbonate at the outset, the nitric acid which is formed unites with further quantities of lime and magnesia, whereby the soil becomes still more depleted of its available carbonates, and hence tends to develop acidic conditions.

274. Nitrogen of sulfate of ammonia fixed by microorganisms. — Nitrogen in ammonia, like that in nitrate

of soda, is subject to more or less fixation by its being taken up by, and becoming a part of the organized structure of, the bacteria, fungi, and other minute plant and animal denizens of the soil.

275. The efficiency of sulfate of ammonia as a fertilizer. — It was concluded by Wagner and Dorsch and has been well substantiated by other experimenters that, as a general rule, nitrogen in sulfate of ammonia possesses about nine-tenths the efficiency of nitrogen in nitrate of soda. The difference of one-tenth may be attributed in part to possible small losses of ammonia by volatilization, but chiefly to the transformation of some of the nitrogen into organic forms, such, for example, as the structure of the organisms which effect its transformation into nitrates. Such a generalization as to the relative efficiency of sulfate of ammonia is nevertheless capable of only restricted application, for with other plants than the cereals, which have been commonly used in such experiments, somewhat different conclusions might be drawn. This is especially true if no account is taken of the possible physiological functions of the soda, especially where the potash supply is deficient. This is plainly shown by a study of a tabulation by Stutzer [1] of a large number of European experiments with nitrate of soda and sulfate of ammonia in which, as far as concerned the cereals, nitrate of soda sometimes gave even poorer results than the sulfate of ammonia. With mangel wurzels and sugar beets, however, the results were almost invariably much in favor of the nitrate of soda. This, as explained elsewhere, may have been due to a correction of the chemical reaction of the soil by the soda of the nitrate of soda, to a conservation of the available potash supply by virtue of soda being

[1] Der Chilisalpeter, Berlin.

taken up in its stead, by the soda having been of benefit to the plants physiologically, or in still other ways.

276. Soda important in trials of nitrate of soda and sulfate of ammonia. — All of the points which have been mentioned emphasize the importance of taking soda into account in comparing the efficiency of the nitrogen in these compounds. A precaution which may be taken is to add to the pots or plots of land which receive the sulfate of ammonia as much sodium carbonate as would be formed from the nitrate of soda. If this precaution is not taken, it becomes doubly imperative to determine by check tests if enough potash is actually present to fully meet the alkali requirements of the plants under experiment. The need of considering the possible effect upon the soil reaction which may be exerted by the residual sodium carbonate derived from the nitrate of soda will obviously be determined very largely by the character of the soil at the outset, and by the adaptations of the plants employed in the experiments.

277. Double decompositions follow the use of ammonium salts. — In the course of the Rothamsted experiments it was found that when ammonium chlorid and ammonium sulfate were applied to the land, chlorin and sulfuric acid began to appear almost at once in the drainage waters, combined with the lime and magnesia which the ammonia had replaced in the soil. As has been explained in another connection, the nitric acid formed in soils as a result of the nitrification of the ammonia may combine with lime, magnesia, or even with potash and soda.

On account of the acid, in combination, in the sulfate of ammonia at the outset, the drain on the lime and magnesia of the soil arising from the use of sulfate of ammonia,

is far greater than that created by the employment of dried blood and other sources of organic nitrogen, which, when nitrified, leave but one acid to be neutralized by the soil bases. Incidentally this tendency to the development of soil acidity by the use of organic nitrogenous materials, just as is eventually the case by the use of sulfate of ammonia, does not appear to have been sufficiently appreciated, and it is usually entirely overlooked.

278. Partial soil sterility sometimes caused by sulfate of ammonia. — Many cases of marked inferiority of sulfate of ammonia as a source of nitrogen had long been on record, but the reason for the very inferior results had not been carefully studied until it was taken up apparently coincidently by Wagner and Dorsch in Germany and at the Rhode Island experiment station. In the year 1890 it was observed at the latter station that sulfate of ammonia was highly toxic, even the first season of its application. At other points in the state of Rhode Island it either became quickly toxic or gave evidence of a tendency in that direction. The experiments of the succeeding three years proved conclusively that this toxic action was due to the creation of an acidic condition of the soil which, either directly or by virtue of toxic substances to which it gave rise, was highly destructive to many varieties of agricultural plants. It was also shown that this condition could be corrected by sodium carbonate, potassium carbonate, caustic magnesia, carbonate of lime, slaked lime, calcium oxalate, and calcium acetate, but that when these bases were combined with chlorin or sulfuric acid, they were usually of no practical value as correctives of the condition. Toward the close of the same decade the experiments by Voelcker at Woburn, England, in which an occasional inferiority of action of the ammonium salts

had already been observed, gave evidence of a highly toxic effect upon barley. This was shown later to have been due apparently to the development of soil acidity, and to be capable of correction by liming.

279. The conditions caused in acid soils by sulfate of ammonia not fatal to all plants. — In the course of the earlier experiments with sulfate of ammonia, at the Rhode Island experiment station, it was found that conditions were produced thereby which were prohibitive of the

FIG. 11. — LIMED GRASSES.
Timothy at left, redtop at right. Sulfate of ammonia. Compare with Fig. 12.

successful growth of lettuce, spinach, beets, Swiss chard, cress, kohl-rabi, cabbage, cauliflower, asparagus, cantaloupes, clover, alfalfa, string beans, peas, vetch, Kentucky blue-grass, timothy, and many other plants. Nevertheless, these conditions failed to interfere with the successful growth of the blackberry, Norway spruce, watermelon, common sorrel, cranberry, and other plants. In fact, several of these latter plants seemed to thrive best of all under conditions which were exceedingly toxic to plants of other kinds. In 1909, after having made sixteen suc-

cessive annual applications of sulfate of ammonia, and after the soil had become still more toxic to most plants, than in the earlier years, it was found that the conditions for the growth of the flowering perennial, *Silene orientalis*, were better than where lime had been used and where, by its application, the conditions formerly toxic to most plants had again been made highly favorable. This emphasizes the fact that any discussion of toxic substances in the soil must embrace a consideration of the particular variety of plant involved.

Fig. 12. — Unlimed Grasses.

Timothy at left, redtop at right. Sulfate of ammonia. Compare with Fig. 11 and note how soil acidity has lessened the proportion of timothy.

The observations at Woburn with a mixture of ammonium chlorid and of ammonium sulfate agree with those made in Rhode Island, with ammonium sulfate, in showing that barley is more sensitive than wheat to the toxic conditions produced. This difference has been attributed by Hall to the deeper rooting habit of the wheat than of the barley, and to a more robust constitution of the wheat plant. Many of the observations made in Rhode Island, in the course of which several hundred different varieties of plants have been tested, fail to support the idea that the different depth of the roots of plants is the chief, or, in some cases, even an important, determining

factor. The results indicate that the explanation of these differences in plants must often be sought in quite other directions. In fact, in the course of the Rhode Island experiments the mangel wurzel, which Hall, in comparison with barley, calls a " deep rooting " plant, was subject to injury in a far greater degree than barley, when sulfate of

FIG. 13. — EFFECT OF TREATMENT ON COMMON SORREL.

Dried blood, sulfate of ammonia, and nitrate of soda, respectively, from left to right. Fertilized alike with potash and phosphoric acid. The more acid the soil was made, the better the growth. Nitrate of soda lessens acidity.

ammonia was used without lime. This difference in the two kinds of plants was not only true of soils where sulfate of ammonia had been applied previously, but also of those poor in lime in many different parts of Rhode Island, and even when nitrate of soda was the only artificial source of nitrogen employed.

280. Sulfate of ammonia an aid in rendering certain grasses dominant. — In connection with the permanent

grass experiments at Rothamsted, it was found that the use of ammonium salts (ammonium chlorid and ammonium sulfate) made the presence of sweet vernal grass (*Anthoxanthum odoratum* L.) and sheep's fescue (*Festuca ovina* L.) prominent, — a fact attributed to the holding of the ammonia in the surface soil and to the shallow rooting habit of these grasses. It has been found, however, at the Rhode Island experiment station that an acidic fertilizer, of which sulfate of ammonia was one constitutent, when used successively upon certain grass plats, has driven out Kentucky blue-grass, clover, and certain other grasses and weeds, leaving red fescue (*Festuca rubra* L.) and sheep's fescue in practically undisputed possession of the land. Where, on the contrary, basic fertilizers have been used, in which the sulfate of ammonia is replaced by nitrate of soda, and acid phosphate by basic slag meal, Kentucky blue-grass, white clover, and other grasses and weeds have almost obscured the fescues. It is also true that these fescues have become dominant on old meadows where natural acidic soil conditions, due to lack of carbonate of lime, inhibit the growth of many other species of grass. It may therefore be questioned whether the shallow rooting is the sole or even dominant factor in the survival of these grasses, and if the chemical reaction of the soil, special ability to utilize ammonia or even unnitrified nitrogenous substances, and resistance to soil compounds which are toxic to other plants, may not be equally important factors.

281. Sulfate of ammonia may cause the suspension of certain bacterial activity. — Sulfate of ammonia, if used to the extent of creating highly acidic conditions in the soil, causes the suspension, at least to a great extent, of the normal bacterial life and gives rise to the growth of molds,

fungi, and doubtless to special types of bacteria suited to the unusual conditions. It was found, for example, in connection with the permanent grass experiments at Rothamsted, that where sulfate of ammonia had long been used, nitrification had practically ceased; and the grass plants were therefore supposedly forced to utilize ammonia or combined nitrogen, instead of nitrates.

The Rothamsted experiments show that barley ripens, and mangel wurzels cease their growth, earlier, when manured with ammonium salts than when grown with the aid of nitrate of soda. This has been explained at Rothamsted as due to the greater descent of the nitrates into the soil and hence to a deeper rooting habit of the plants, induced thereby, especially in dry seasons, on which account the plants are better supplied with water. The Rothamsted experiments show, nevertheless, that in such dry seasons sulfate of ammonia acts relatively better than in wet ones, due supposedly to higher soil temperatures, to better aëration, and hence to a better chance for nitrification. On this account, in moderately dry seasons, the ammonia would be expected to nitrify rapidly, and when so nitrified it is as movable in the soil as the original nitrate; hence the preceding explanation would not seem to be adequate in all cases. In fact, it seems probable, in view of the possible lack of potash and of the now well-established plant food value of soda under such circumstances, especially for mangel wurzels, that the soda itself may have been a factor in keeping up the longer growth and also in causing the usually greater crop.

Experiments by Maercker, and by Wagner and Dorsch, show that barley is relatively more responsive than the other cereals to nitrate of soda. Wagner also observed that barley is dependent, to a far greater degree than oats,

upon potash manuring. On aeeount of this fact, he explains that the better aetion of nitrate of soda than of sulfate of ammonia, upon barley, is due to the fact that the soda comes more into play by way of performing a part of the functions of potash.

282. Sulfate of ammonia liberates plant food. — Aeeording to the aeeepted idea that the ammonia of sulfate of ammonia ean replaee lime, magnesia, potash, and soda, when the latter are held in zeolitic eombinations in the soil, it is evident that the use of sulfate of ammonia is likely to result in the liberation of these plant food ingredients; and if employed in exeess without other fertilizers, it may finally result in seriously impoverishing the soil. This faet is fully substantiated by the studies of drainage waters made by Voeleker and by Lawes and Gilbert. The compounds which were chiefly inereased in the drainage waters, upon the applieation of ammonium salts, were ehlorids, sulfates, and ealeium nitrate. It was found that 400 pounds of sulfate of ammonia removed from the soil annually in this way about 172 pounds of lime.

283. Ammonium salts fleeting in their effects. — Notwithstanding that ammonia enters readily into zeolitic and other ehemieal eombinations in the soil, it is not capable of being continuously held for suceessive years. This is shown by experiments at Rothamsted in whieh mineral fertilizers were alternated through a long series of years with ammonium salts; for in the alternate years when only mineral fertilizers were applied, the yield averaged about the same as where the same mineral fertilizers were used eontinuously without any ammonium salts. These results further support the faet of the rapid transformation of the ammonia into nitrates in the soil. They

also show that the same care must be exercised in the employment of the ammonium salts as in the application of nitrates, in order that no more may be applied than will be utilized in the same season.

It was found by Voelcker, Frankland, and others that the larger the application of ammonium salts in the spring, the greater were the losses of nitrates in the drainage water the following December. The loss which resulted in this way was found to amount to 8.5 pounds of nitrogen per acre for each inch of rainfall lost by leaching. After an autumn application of ammonium salts at the rate of 600 pounds per acre, Frankland found the loss of nitrogen equal to 18 pounds per acre for each inch of rainfall lost by percolation.

284. Ammonium salts leach less quickly than nitrates. — Even if the employment of considerable amounts of ammonium salts in the autumn has been found to be uneconomical, it is nevertheless true that in making spring applications the danger of immediate losses by leaching are less, in the case of ammonium salts, than in connection with nitrates.

285. Ammonium sulfate may cause injury on light calcareous soils. — It was observed by Dehérain at Grignon, France, that on light calcareous soils an efflorescence of calcium sulfate followed applications of ammonium sulfate, after a few days of drought. The physical condition of the soil was so seriously injured in consequence, that the ill effects of drought were much heightened, and, furthermore, the injury lasted for several seasons. On soil of the same character, nitrate of soda was nevertheless highly beneficial.

For several reasons Dehérain has recommended the restriction of applications of ammonium salts to stiff or

heavy land, and even then to quantities ranging from 140 to 175 pounds per acre.

286. Ammonia may injure plants. — It appears to be well established that sufficient ammonia may enter the plant to exert a granulating or coagulating effect upon the protoplasm, a result which is inimical to plant life. Nevertheless, Hosäus, Adolf Mayer, and others have found small amounts of ammonia present in normal plants, and Mayer has demonstrated that plants can utilize nitrogen in ammonia, though probably not as safely and successfully in most instances as when it is taken up from nitrates. There are, nevertheless, certain classes of plants that probably take up their nitrogen chiefly or almost wholly in ammonia and in still higher soluble nitrogenous compounds, for they thrive splendidly in locations where nitrification is practically suspended. The foregoing applies even to plants which are not supposed to derive their nitrogen through the aid of symbiotic bacteria or through the possible intervention of mychorhiza.

A reason advanced for the usual better action of nitrates than of ammonium salts is that even if the former are reduced to ammonia in the soil, the change takes place so gradually that the resultant ammonia does not accumulate in sufficient amounts to cause injury. The ammonia in such cases is built up through successive stages into the final nitrogenous compounds of the plants, practically as rapidly as it is formed.

Experiments by Lehmann and others show that in some cases nitrates are apparently preferable in the early stages of the growth of certain plants, whereas, later, ammonia gives better results; nevertheless, in the case of still other kinds of plants these conditions were exactly reversed.

287. Calcium cyanamid a new product. — A nitrogenous fertilizer which has been rendered possible by the recent electrical development is calcium cyanamid, known commercially as "nitrolime" "nitrolim" and "lime-nitrogen," and in Germany as "Kalk-stickstoff."

288. The manufacture of calcium cyanamid. — The process for the manufacture of calcium cyanamid, which was placed on a commercial basis by Frank and Caro of Berlin, Germany, is based upon the employment of calcium carbid, which combines readily with nitrogen gas at moderate temperatures, yielding the calcium cyanamid

$$(CaC_2 + N_2 = CaCN_2 + C).$$

calcium carbid — nitrogen — calcium cyanamid — carbon

The calcium cyanamid in turn may be completely decomposed by steam at high pressure, yielding ammonia and calcium carbonate

$$(CaCN_2 + 3\ H_2O = 2\ NH_3 + CaCo_3).$$

calcium cyanamid — water as high pressure steam — ammonia — calcium carbonate

Thus it may be used in the manufacture of ammonium salts.

In the practical carrying out of the process, the calcium carbid is ground coarsely and is then placed in iron tubes through which, while subjected to heat, a current of nitrogen gas is passed.

It is possible to produce the carbid and cyanamid simultaneously, but in actual practice it has been found preferable to separate the processes.

The preparation of the nitrogen gas which is required, may be accomplished by passing air over red-hot copper. The oxygen combines with the copper to produce copper

oxid, thus leaving the nitrogen gas behind. The copper oxid is then reduced by passing over it, while hot, a current of coal gas.

Nitrogen gas is more commonly obtained for the purpose of the manufacture of calcium cyanamid by the fractional distillation of liquid air. In this process the oxygen is separated from the nitrogen, the former being then utilized for various other purposes.

The first works for the extensive manufacture of calcium cyanamid were established by an Italian company, the Società Generale per la Cianamide, of Rome, which in turn embraces two companies organized for distinct purposes. Works have already been established in several different countries, including two in the United States.

It is claimed that one electrical horse power is capable of fixing 772 kilograms of nitrogen per annum, but the yield actually secured in practice is only from 300 to 330 kilograms.

289. Changes in calcium cyanamid resulting in the soil. — The calcium cyanamid is a light, fine, dark gray powder. Owing to its high content of calcium oxid, it readily takes on water until the lime is slaked. At the same time the calcium cyanamid itself slowly decomposes, according to the reaction indicated above, with gradual liberation of ammonia.

The views as to the changes taking place in cyanamid in the soil have undergone more or less modification. It is now asserted that the first change which takes place is the formation of urea

$$\underset{\text{calcium cyanamid}}{(CaCN_2} + \underset{\text{water}}{H_2O} = \underset{\text{calcium hydrate}}{Ca(OH)_2} + \underset{\text{urea}}{CO(NH_2)_2}),$$

and that the urea then breaks up through bacterial agencies, forming ammonium carbonate, which by nitrification is transformed into nitric acid. The nitric acid reacting finally with the calcium carbonate results in the production of calcium nitrate, though of course the formation of other nitrates is also possible.

290. The utilization of calcium cyanamid for the manufacture of urea and other substances. — It has also been found that calcium cyanamid may be utilized in the practical manufacture of urea; it has likewise been employed in the production of guanidin; and even of creatin, one of the substances present in human muscle and found in meat extract.

291. Calcium cyanamid as a fertilizer. — As a fertilizer, calcium cyanamid compares well in efficiency on heavy soils with sulfate of ammonia, but it has been found to be more or less toxic to young plants, due supposedly to the formation at the outset, through the action of water, of some dicyanamid. Such injury is said to be avoided if it is introduced into the soil long enough in advance of the time of seeding or planting. Calcium cyanamid has the advantage over sulfate of ammonia for acid soils, of having an ultimate basic, rather than acidic, effect.

292. Practical difficulties connected with calcium cyanamid. — In order to remove some of the difficulties connected with the losses of ammonia, to facilitate handling, and for other reasons, it has been proposed to mix with the calcium cyanamid a small quantity of peat, but there are objections to such a plan, in view of the additional cost of transportation. The product as manufactured and sold in the United States, for a time, was said to be subjected to an additional treatment, the object of which was to increase its stability and thus obviate the possible loss

of ammonia. In one of the processes the lime was fully slaked, and nitrate of soda was said to be introduced during the process to keep down the temperature. It has also been proposed to treat the material with sulfuric acid to a limit which would prevent the tendency to decompose with loss of ammonia. Finally, it has been stated that the plan of minimum hydrating has superseded the latter process. In any event, the calcium cyanamid industry is at present probably only in its infancy, and the recent difficulties connected with its more general utilization in the great fertilizer manufacturing industry will doubtless be more fully overcome in the near future.

293. The output of calcium cyanamid. — The production of cyanamid in the United States had reached in 1912 a limit of 12,000 tons per year at the factory in Niagara Falls, and other works are likely soon to add greatly to the output.

The total sales of cyanamid are claimed to have risen in two years to 4,000,000 tons per annum.

CHAPTER XV

NATURAL PHOSPHATIC FERTILIZERS

Phosphorus is said to have been discovered in 1669 by the alchemist Brandt, a merchant of Hamburg, while searching in urine for the philosopher's stone. It was also discovered independently by the chemist Kunkel, of Berlin, and in 1688 it was extracted by Albinus from the seeds of the mustard and cress.

The discovery of phosphoric acid was made by Margraff in 1743, who by calcining it with charcoal reconverted it into phosporus.

It was not until 1769 that Gohn, a Swedish chemist, found phosphoric acid in bones; and a little later the Swedish chemist Scheele developed a practical process of recovering the phosphorus from them.

It was not until more than a century after phosphorus was discovered that its mineral nature was ascertained by Gohn, who found it in pyromorphite, a lead phosphate. Soon thereafter the discovery of the presence of phosphorus in the mineral apatite was made by Vauquelin and Klaproth.

294. Bone as a fertilizer. — The use of bone as a fertilizer is such an ancient practice that it is now impossible to establish definitely when or where it had its origin. Its employment is mentioned by many English writers from 1653 to the beginning of the last century, and in England the value of bone as a fertilizer came to be generally recognized much earlier than anywhere on the continent of Europe. In fact, it is recorded that machines for grinding

bone were already in use in England by 1778, though they were obviously crude and not calculated to reduce the material to the same degree of fineness, as modern mills.

As early as 1815 the English supply of bones had become so inadequate that they were imported from the continent of Europe in ever increasing quantities, the importations soon reaching 30,000 tons per annum. It has been stated by Liebig that even the battle-fields of Leipzig, Waterloo, and the Crimea were turned up by the English in their search for bones.

According to Heiden, the value of bone as a fertilizer was not generally recognized in Germany until from 1855 to 1885.

With the discovery of other phosphates the importations of bone into England became less, but they have again increased; for as late as 1907 it was reported that 46,115 tons were brought into England in a single year. Of this quantity 32,800 tons came from Argentina and India, and the rest from other countries.

295. The chemical composition of bone. — The composition of bone varies in different parts of the same animal, according to its age, health, and sometimes also with the character of food which it has consumed. There is also a variation in the composition of bones, similarly located, in the different kinds of animals. Bone is composed of both mineral and organic matter. The former is assumed to consist chiefly of tricalcium phosphate

$$(Ca_3(PO_4)_2 \text{ or } Ca\langle \begin{matrix} O \\ O \end{matrix} \rangle \overset{\overset{O}{\|}}{P} - O - Ca - O - \overset{\overset{O}{\|}}{P} \langle \begin{matrix} O \\ O \end{matrix} \rangle Ca),$$

though it also contains very small quantities of magnesia and fluorin. In the case of bones which are not care-

fully prepared, traces of fluorin, sodium, and iron are frequently found which are present in slight residues of blood.

The organic matter of the bone includes ossein, collagen, and chondro-mucoid. The ossein when dry contains about 17 per cent of nitrogen and may be converted by long heating with water into glue and gelatine. The following statement by Murray shows quite fully the constituents and average percentage composition of the fresh bones of mammals: —

			Per Cent	
Water	6.7		6.7	
Organic matter	40.0	fat	14.6	
		ossein	25.4	= 4.0 nitrogen
Ash	53.3	P_2O_5	22.3	= 48.7 $Ca_3(PO_4)_2$
		CaO	29.2	
		Mg. F, etc.	1.8	
	100.0		100.0	

296. Composition of the ash. — When bones are burned, only the mineral matter remains behind, and this is known as bone ash. If bones, on the other hand, are treated for a long time with dilute hydrochloric acid, the mineral matter is dissolved and the organic framework of the bone remains, still possessing its original form.

297. Composition of weathered bones. — In the case of bones which have been burned for a time, or which have lain exposed to the weather, considerable of the organic matter has been lost, and they are therefore poor in nitrogen, but richer in phosphate than fresh bone.

298. Treatment of bone for the removal of fat. — The treatment of bones for the removal of fat may consist in boiling, steaming at high pressure, or extraction with naphtha or other solvents. The fat is in such demand and has such a high commercial value that it is now

usually removed from bones, more or less completely, before they are marketed for fertilizer purposes. The bones are ground and sold as fine or coarse ground bone, according to the degree of fineness. Such bone usually contains from 1.5 to 4 per cent of nitrogen.

After the extraction of the fat by means of a solvent, or by boiling in water, bones are sometimes subjected to high steam pressure for the removal of gelatine. In some cases, also, the bone is treated directly with steam at high pressure, which removes most of the fat and much of the ossein in a single operation. After bones have been steamed in this manner, they crumble readily and can be ground with ease to a fine powder. The material is sold in this country under the name of " fine-ground steamed bone," although the designation " steamed " is often omitted.

299. Effect of steaming on the nitrogen content. — Bone, if subjected to severe steaming, may not contain more than from 1 to 1.5 per cent of nitrogen instead of from 2 to 4 per cent, as would otherwise be the case. On account of the removal of so much of the organic matter in such cases, the content of phosphoric acid may rise to from 27 to 30 per cent, which is from 5 to 6 per cent above the amount usually found in commercial bone.

300. Bone wastes from industries. — Bone is used for the manufacture of buttons, knife handles, and a vast number of other articles; the wastes from which are ground and sold as bone meal or are used in compounding commercial fertilizers.

When bone is subjected to destructive distillation, animal charcoal, containing about 10 per cent of carbon, is produced, in a manner analogous to the production of wood charcoal from wood. This material is employed in sugar

refineries for clarifying sugar solutions, and when no longer fit for such use it is either reduced to bone ash, or it is treated with sulfuric acid. By the latter process the bone-black is transformed into a superphosphate known commercially as "vitriolated" or "dissolved" bone-black.

Bone is sometimes used in the process of annealing, as a result of which it loses much of its nitrogen and becomes highly carbonized, consequently closely resembling bone-black. Such material, though occasionally sold for use directly as a fertilizer, should preferably be treated with sulfuric acid before its application to the soil.

301. Fermentation and other methods of disintegrating bone. — In England and elsewhere bones are sometimes moistened with water and allowed to ferment in heaps, which process renders them more available.

Bones have also been treated in tanks with urine from cow stables which causes them to gradually soften and disintegrate.

The process of steaming increases greatly the solubility of bone in ammonium citrate, and it is usually conceded to greatly increase the availability of the phosphoric acid to plants, though it has been found by Kellner, in Japan, in a moist and hot climate, that bone before steaming was even more available than afterwards.

302. Bone meal as a fertilizer. — The most ideal soils on which to use "undissolved" bone meal, whether steamed or raw, are those which are open and inclined to be sandy or gravelly, though they should not be too dry. On the other hand, bone acts more slowly on heavy clay and silt soils.

For many years bone meal was the favorite fertilizer of the American farmer, not only on account of its well-known power to immediately increase crops to a consider-

able extent, but chiefly because of its accredited lasting qualities. (See Fig. 14.)

In recent years the use of acid phosphate and of other superphosphates has increased to such an extent as to keep bone down to a price which still admits of its frequent agricultural use. At the same time, on account of the greater demand for vegetables and for early garden crops, which must reach a marketable stage in the shortest possible time, many farmers have come to a realization of the fact that it is often better economy to expend money for quick-acting acid phosphate rather than to tie up in the soil, for some years, a large investment in bone.

Bone meal is a favorite substance for application before seeding land to clover and grass. It is also much used for fruits, hops, and for crops which require a long season in which to mature.

If bone meal is applied continually for many years to a soil in need of liming, it very gradually tends to correct the condition; but not rapidly enough to justify waiting for it to do this work. In fact, basic slag meal is far more efficient in this direction than bone meal, and it is at the same time a more quickly available phosphate.

For plants and soils which need liming, it is always more economical to lime the land at the outset, no matter what the form of phosphate to be used, than to wait for the phosphate to gradually correct the existing conditions.

303. The soluble and reverted phosphoric acid of bone. — Ground raw bone and steamed bone rarely yield much more than 0.5 per cent of "soluble" phosphoric acid upon long and thorough leaching with distilled water, and raw bone is but slightly soluble in neutral ammonium citrate solution, at the usual temperature of 65° C.

FIG. 14. — LIMED AND UNLIMED POTATOES.

Both fertilized with muriate of potash and nitrate of soda. Showing after effects of *fine ground steamed bone.* Same amount of phosphoric acid as in Figs. 15–23.

at which "reverted" phosphoric acid is determined. Steamed bone, on the contrary, yields a considerable percentage of reverted phosphoric acid, which, added to the soluble, makes up the "available" phosphoric acid reported by analysts. It is probable that the reverted or available phosphoric acid of bone is nevertheless not so readily utilizable by plants as "back-gone," or true reverted phosphoric acid (dicalicum phosphate), which is produced by the direct action of lime or of tricalcium phosphate upon soluble phosphoric acid (monocalcium phosphate).

304. Bone tankage. — Bone tankage contains widely varying percentages of phosphoric acid and nitrogen, ranging from 9 to 20 per cent of the former and usually from 4 to 8 per cent of the latter.

What has been said of steamed bone applies to the tankage produced by subjecting the waste bones of slaughterhouses and meat markets to the action of superheated steam. It is not infrequently the case that as much as one-half of the total phosphoric acid of such tankage is rendered soluble upon treatment in the conventional manner with neutral ammonium citrate solutions at 65° C., and it hence appears in the statement of the analysis as reverted phosphoric acid. What has been said of the use of bone in the previous section applies equally to the practical employment of tankage.

305. Fish as a source of phosphoric acid. — The refuse fish from the menhaden oil factories often contain, in addition to the 6 to 8 per cent of nitrogen, from 5 to 7 per cent of phosphoric acid. Fish heads and skeletons from fish works are often still richer in phosphate. Such fish wastes are often dried, ground, and sold directly to farmers; they are also introduced into commercial fertilizers,

especially in the manufacture of the goods sold under the name of "fish and potash."

306. The nature of floats. — The name "floats" was given originally to an especially fine dust product which was formed in connection with the ordinary grinding of phosphate rock, but it is now often applied to any finely ground, unacidulated tricalcium rock phosphate.

307. Soils on which to use floats. — This phosphate is especially applicable on peat or muck soils, as has been abundantly demonstrated in the course of the experiments on the renovation of the acid peat (Hochmoor) soils of northern Germany. Next to peat and muck soils, this material is useful on such upland soils as are exceptionally rich in acid vegetable matter. The profitable use of such phosphates has been especially pointed out by Hopkins in his work with the black soils of the Illinois corn belt. This phosphate is much less applicable on light, open, sandy, and gravelly soils than on those previously mentioned.

308. The action of manure on floats. — According to pot experiments by Hartwell and Pember [1] and to experiments by The. Rémy,[2] the mixing of the raw tricalcium phosphate with stable manure and decomposing materials does not materially increase its efficiency. In fact, the field experiments at the Ohio station which have been frequently cited elsewhere to prove the contrary were not conducted in such a manner as to furnish positive evidence on this point either pro or con. It still remains to be conclusively demonstrated that floats are rendered more effective by being introduced either into the manure directly or by scattering them in the gutters behind the farm animals.

[1] Bulletin 151, R. I. Station.

[2] Bonn. Landw. Jahrb., *40*, 559–611 ; Abs. Chem. Abstracts, *6*, 1048.

309. How floats should be used. — It is true of floats, as of other rather insoluble phosphates, that the best way to apply them is to incorporate them thoroughly with the soil; for their availability is affected not only by the carbonic acid brought into the soil by the rain and produced therein by the decay of vegetable matter, and by contact with acidic matter in the soil, but also by the nitric acid resulting from active nitrification.

Floats are obviously most applicable to those plants which have a long season of growth, and least of all for such garden or trucking plants as must be pushed rapidly to maturity. In the latter case the crops must not only reach the market at the earliest possible moment, but the growth must be rapid in order that they may be tender and acceptable to the consumer. Again, floats are less applicable for those plants which possess a low feeding power for phosphoric acid, such as the turnip, cabbage, and certain other similar plants, than for crops possessing a greater feeding power, as, for example, Indian corn, millet, clover, and certain grasses. Indeed, this difference in the requirement for readily available phosphoric acid has been well established by field experiments at Rothamsted, by many European experimenters, and by Brooks and others in the United States.[1] Nevertheless, it is claimed that certain of the cruciferous plants can utilize raw phosphates better than either the oat or vetch can utilize them.[2]

310. Liming in connection with the use of floats. — The advice is often given never to lime land to which floats are to be applied on the ground that the lime, if freshly burned or hydrated, will absorb carbonic acid

[1] See Buls. 114 and 118 Agr. Expt. Sta. of the R. I. State College.

[2] Centralb. f. Agrikulturchemie, *39* (1910), 495.

which might otherwise serve to attack the floats and render them more available. Another reason often given is based upon the known greater solubility of calcium carbonate than of tricalcium phosphate in carbonic acid. On this account the carbonic acid would be expected to be utilized in dissolving calcium carbonate, before it would attack the tricalcium phosphate to an appreciable extent. Admitting that this might be sound advice as concerns a soil already well supplied, naturally or artificially, with reasonable amounts of calcium carbonate, it does not, nevertheless, apply in all cases on such soils as are naturally deficient in calcium carbonate, especially if they are of a quite acid character. In order to make this point plain, it should be stated that a soil may be so acid that given varieties of plants will not thrive well upon it, and hence no matter how much phosphoric acid is made available by the action of carbonic acid, nitric acid, or otherwise, the plants cannot utilize it, because another factor has become the one which limits growth. Under such circumstances, therefore, enough lime must be applied to make the soil a suitable habitat for the plant, even though upon theoretical grounds, and without reference to the plant to be grown, the omission of lime would seem to be advisable. If, on the contrary, plants are grown which, like golden millet, serradella, and certain lupines, thrive well on acid soils, the advice about avoiding the use of lime, even on moderately acid soils, might nevertheless be sound. (See Fig. 15.)

311. Apatite or phosphorite. — The terms "apatite" and "phosphorite" have come to be used interchangeably, although the latter is the term preferred for commercial purposes.

Distribution in soils. — Apatite is a phosphate which is

FIG. 15. — LIMED AND UNLIMED POTATOES.

Both fertilized with muriate of potash and nitrate of soda. Showing after effect of *floats*. Same amount of phosphoric acid as in Figs. 14 and 16–23.

widely distributed in minute crystals in most soils, and especially in rocks of igneous origin. This phosphate has probably been the source of the phosphorus in the organic matter, and in other combinations, in most soils of such derivation. It has been assumed that in many cases minute crystals of apatite are formed in the soil under normally existing conditions, although laboratory experiments made in the attempt to produce them, in a wet way, have thus far failed.

312. The chemical composition and occurrence of apatite. — The pure crystals of apatite are usually blue or green, although they may be gray, white, and transparent. The mineral, if pure, is a fluor-apatite corresponding closely to the formula $3\ Ca_3P_2O_8 + CaF_2$. Occasionally, however, the fluorin is wholly or partially replaced by chlorin, in which case the apatites are lighter in color and are designated as chlor-apatites. The pure fluor-apatite contains about the equivalent of 92.25 per cent of tricalcium phosphate, and 7.75 per cent of calcium fluorid. A sample of Norwegian apatite examined by Voelcker was found to have the following composition:—

	Per Cent
Tricalcium phosphate	90.07
Calcium chlorid	6.13
Calcium fluorid	2.54
Oxid of iron	0.29
Alumina	0.38
Potash and soda	0.17
Water	0.42

Apatites are found in several places in Renfrew and Lawrence counties in Canada, where beautiful large crystals occur, likewise in the Province of Estramadura, Spain. They also occur in Portugal, Norway (near Christiania), and elsewhere. Apatite is often found in veins

mixed with quartz, as nodules in certain sand-stones, in carboniferous slates, and as cementing material in rocks. Many of the apatites occur in massive or amorphous forms.

For several years the apatites of Canada, containing the equivalent of 80 to 86 per cent of tricalcium phosphate, those from Norway, containing the equivalent of 70 to 90 per cent of tricalcium phosphate, and the deposits in Spain, containing the equivalent of from 70 to 85 per cent of tricalcium phosphate, were worked quite extensively; but these phosphates have since been largely replaced by those from Algeria, Florida, Tennessee, and from many other sources. At present renewed interest in them is being awakened in view of their possible utilization by the process of Palmaer (see Section 340).

When apatite is reduced to a powder and is subjected to the action of pure water, the resulting solution gives an alkaline reaction with phenolphthaleïn or litmus, whereas the ordinary tricalcium phosphates yield an acid solution with the same indicators. The solubility of apatite is about seven times as great in a saturated solution of carbon dioxid as in water, but even then more lime than phosphoric acid is dissolved. The presence of even a small amount of carbonic acid in solution also increases its solubility.

313. Wagnerite. — The mineral Wagnerite is a magnesium fluor-apatite corresponding to the calcium fluor-apatite. There exists also a corresponding ferrous salt known as triplite, but neither of these is of importance as a soil mineral or from the fertilizer standpoint.

314. Coprolites. — The term "coprolite" from two Greek words meaning "dung" and "stone" was given by Buckland to certain peculiarly shaped stones found in the Lias marls chiefly at Lyme-Regis and also near Bristol,

England, which were said to resemble fossil fir cones. They are from 2.5 to 4 or even in extreme cases 8 inches in length, somewhat flattened, and ranging in color from ash gray to black. The coprolites were found in deposits with remains of the *Ichthyosaurus* and the bones and teeth of fish, which coupled with the fact that their structure resembled that of fossilized animal excreta, led to the belief that they were chiefly the excreta of reptiles of the extinct group of saurians. The term "coprolites" was, however, also applied to phosphates which are now known to be of undisputed concretionary character. The latter have also been called pseudo-coprolites in order to distinguish them from those of fæcal origin.

Coprolites are by no means confined to England, for they occur in France, Russia, and elsewhere.

The concretionary origin is supposed to be the result of the replacement of the carbon dioxid of calcium carbonate by phosphoric acid, in the presence of moisture and vegetable matter.

The coprolites are usually associated with considerable calcium carbonate, also with calcium fluorid, oxids of iron, alumina, silica, and small amounts of organic matter. They usually contain from 50 to 60 per cent of tricalcium phosphate.

315. Phosphatic guanos. — Where birds deposit large quantities of excreta in humid locations the material gradually loses its nitrogen until the residues finally become mineral phosphates.

The Island of Lobos yields a guano with only from 2 to 3 per cent of nitrogen. This represents a stage between the true guano with a high nitrogen content and these true phosphatic guanos. These phosphates often contain, as might be expected, traces of nitrogen and alkalies,

but the amounts are too small to be of any practical account.

Such guanos often contain from 70 to 80 per cent of tricalcium phosphate and usually but small quantities of iron and aluminum. These characteristics, and the ease with which they can be pulverized, make them well adapted to the manufacture of superphosphate.

The phosphatic guanos known as Aruba, Navassa, Sombrero, and Curaçao are found in the West Indies. The Mejillones guano comes from Bolivia, and large quantities have been found on the Baker, Abrolhos, Christmas and Oceanic islands in the Pacific, and elsewhere. Some of these guanos have an average content of 80 to 85 per cent of tricalcium phosphate. Many of the original deposits have been exhausted, but the phosphate is still being imported from the Oceanic and Christmas islands, and from a large number of other islands of the Pacific.

Clipperton Island in the open sea off the coast of Brazil is covered with a bed of phosphatic guano six feet deep. It contains from 83 to 86 per cent of tricalcium phosphate and only traces of iron and alumina.

316. Nassau or Lahn phosphate. — The so-called Nassau or Lahn phosphate is found in Germany and these deposits were worked extensively following their discovery in 1864. They contain from 35 to 70 per cent of tricalcium phosphate; but such large amounts of iron and alumina are present as to make them objectionable for the manufacture of superphosphate. Germany has at present practically no workable phosphate deposits.

317. French, Belgian, and Portuguese phosphates. — The Departments of Pas de Calais, Somme, and Oise, in France, contain valuable deposits belonging to the Cretaceous period; and many other sections of the country

also contain very extensive deposits, though often in thin beds.

Phosphate deposits at Mesvin and at Cipley near Mons, Belgium, have been worked extensively. The lower grades from these deposits contain from 25 to 30 per cent of tricalcium phosphate. The better grades, which occur chiefly in pockets, contain from 45 to 60 per cent of tricalcium phosphate. This phosphate is light brown and has practically the appearance of oölite. It crumbles easily and owing to its peculiar structure it has at times been imported into the United States in small amounts for use as a drier in mixed fertilizers, in order to make them more drillable.

Other phosphate deposits exist in the district of Liége and elsewhere in Belgium.

Phosphates somewhat similar to those of Cipley have been found in France, Portugal, and elsewhere and, although they are often quite rich in tricalcium phosphate, they contain clay and marl in quantities objectionable from the standpoint of the superphosphate manufacturer. An exception is however afforded by the Somme phosphates of northern France which are richer in tricalcium phosphate, and contain less iron and aluminum oxids. In utilizing them for the manufacture of superphosphate it is considered desirable or necessary to employ hot rather than cold sulfuric acid.

318. The phosphates of Russia and Northern Africa. — In Russia there are large numbers of phosphate deposits, the best of which are in central Russia. They are distributed over an area estimated at 50,000,000 acres.

One of the chief sources of phosphate for Europe, at present, is the great deposit supposed to stretch practically across the northern part of the continent of Africa, though

Morocco has not as yet been carefully examined. The centers of export are Algeria and Tunis from which approximately two millions of tons are now shipped annually.

The amount of tricalcium phosphate usually present in the material as exported is about 60 per cent, but by careful selection it may run as high as 70 per cent.

The beds thus far explored in Egypt yield a phosphate containing only from 40 to 50 per cent of tricalcium phosphate, which is too low for present profitable exportation. These deposits underlie the Eocene; and the phosphate-bearing strata usually range from 7 to 10 feet in depth.

One great advantage of these phosphates is that they contain only little iron and alumina. When used in an unacidulated form in comparison with the Florida phosphate, on the Hochmoor (acid peat) soils of northern Germany, they have been reported as being superior to the American product.

319. The phosphates of South Carolina. — Until within the last twenty years the main source of phosphate for the United States was South Carolina. The chief supply for Europe came also from the same source until the discovery of the high grade African deposits. Many of these phosphates are essentially nodular and belong at the bottom of the Eocene period; others consist of phosphatic limestones alternating with the nodular deposits. The material resembles somewhat that at Cipley in Belgium. Associated with the phosphates, in the beds of marl, are teeth and bones of sharks. The phosphate, however, has been redeposited from solution in carbonic acid and in organic acids, and is still being formed.

The so-called " river " phosphate was secured by dredging the bottoms of rivers, whereas the usual methods of mining prevail in connection with the land phosphates.

The former contain usually about 60 per cent of tricalcium phosphate, but they are preferable for the manufacture of superphosphate to the richer (70 to 80 per cent) land phosphate on account of their containing less iron and aluminum oxids.

320. The Florida phosphates. — The discovery of phosphates of the Oligocene period in Florida in 1887, followed by their extensive exploitation, focused the attention of the entire world upon them.

The black, river, pebble phosphate containing 60 to 70 per cent of tricalcium phosphate was formerly dredged in large quantities from beds of streams, but such mining in the Peace River district has now been abandoned.

The land pebble phosphate, which bears much resemblance to calc-sinter, is found in Florida in large quantities; and the output has reached as much as 1,250,000 tons per annum. It is consumed chiefly in the United States. It contains from 66 to 75 per cent of tricalcium phosphate and an average of 2.3 per cent of iron and aluminum oxids, though the latter usually fall below 2 per cent. The masses are rounded, flattened and of a yellowish to white color and occur associated with occasional stringers of quartz sand. The deposits resemble gravel beds in certain respects.

The better grades of land phosphate, to which the terms "rock" and "bowlder" phosphate are applied, vary less in composition than the pebble phosphates and are sold on a guaranty of 77 per cent of tricalcium phosphate, but they not infrequently contain as much as 80 per cent. This is much in excess of the amount in the South Carolina phosphate. They frequently, however, contain as much as 6 per cent of iron and aluminum oxids which is a highly objectionable feature.

Soft phosphate. — The Florida "soft" phosphate, containing from 25 to 70 per cent of tricalcium phosphate and 3 to 7 per cent of iron oxid and alumina, is usually associated with such large quantities of calcium carbonate or earthy matter, as to render it unsuitable for the most economical manufacture of superphosphate. For this reason it has been ground and utilized to a considerable extent for direct application to the land, and likewise as a drier in the manufacture of commercial fertilizers.

321. The Tennessee phosphates. — Upon the discovery of the great phosphate deposits of Tennessee in 1894, following closely upon those in Florida, it was considered that inexhaustible supplies were at hand; the quantity mined has, however, reached from two to three million tons per annum and it is now estimated by the U. S. Geological Survey that the exhaustion of these deposits will be accomplished in another generation, if the mining increases at as great a rate as is to be expected.

322. Phosphates of the Western States. — In view of the rapid exhaustion of the phosphate beds of the eastern United States, the recent discovery of high grade phosphate fields in Idaho, Wyoming, and Montana, which are now believed to be the greatest thus far discovered in the world, is hailed with great satisfaction by those interested in the future prosperity of the United States. In each of the nine townships thus far examined it is estimated that there are not less than 60,000,000 tons of high grade phosphate rock, and in one of the townships the estimate reaches 293,000,000 tons.

The preceding estimates do not embrace 34,000 acres of Montana phosphate beds previously withdrawn from the lands opened for settlement. These figures are especially significant when one recalls that but about 39,000-

000 tons of phosphate rock have thus far been mined in the United States.

Certain of these western deposits are situated reasonably near great copper smelters which are capable of producing enormous quantities of sulfuric acid as a cheap by-product, so that the conditions are especially favorable for the manufacture of acid phosphate or of other even richer products. In the case of some of the latter the cost of transportation, per unit of phosphoric acid, would be but one-third of the cost in ordinary acid phosphate.

323. Occurrence and composition of certain aluminum phosphates. — Aluminum phosphate, associated with some iron phosphate, is found on the Islands of Grand Connetable, a French possession on the coast of French Guiana; on the Island of Redonda (where the mineral redondite occurs), near the Island of Montserrat in the British West Indies; and on the Islands of Alta Vela, Sombrero, and Navassa. The material from the Island of Redonda often contains as much as 35 to 36 per cent of phosphoric acid, combined almost wholly with alumina. It may nevertheless contain in some cases as little as 20 per cent of phosphoric acid. The phosphates from Alta Vela, Sombrero and Navassa, contain about 22, 31, and 31 per cent of phosphoric acid, respectively.

Wavellite. — The mineral Wavellite is a crystallized aluminum phosphate ($3\ Al_2O_3 \cdot 2\ P_2O_5 \cdot 12\ H_2O$) which, though possibly formed in a wet way, is supposed by certain writers not to be generally present in soils.

324. Roasting increases the efficiency of aluminum phosphate. — The efficiency of these phosphates is greatly increased by subjecting them to a roasting process. This fact is not new but it has been recently well shown in trials of the roasted and unroasted product, at the experi-

ment station of the Rhode Island State College,[1] and later in the course of experiments by Fraps. The Rhode Island experiments have shown in a most striking manner the effect of slaked lime in increasing the crop-producing efficiency of the roasted, in contrast with the unroasted, Redonda phosphate. Furthermore, this effect continues for several years after the last application of each substance is made to the soil. (See Figs. 16 and 17.)

325. The solubility of artificial aluminum phosphate. — The solubility of artificial aluminum phosphate appears, according to Gerlach, not to be increased by the presence of carbon dioxid in solution, even in the presence of lime and magnesia, but its solubility is greatly increased by sodium and potassium hydroxids and in a lesser degree by free mineral acids. As concerns oxalic and citric acids, they differ but little in their solvent action upon the phosphoric acid of aluminum phosphate, and both are far superior in this respect to acetic acid. The presence of aluminum hydroxid while lessening the solvent action of acetic acid had no effect upon the action of citric and oxalic acids.

According to Schneider[2] both aluminum chlorid and aluminum sulfate, which give acid solutions, increase the solubility of aluminum phosphate.

The action of water upon several artificial preparations of aluminum phosphate of varying degrees of basicity, has been determined by Cameron and Hurst,[3] from which it appears that the total quantity of phosphoric acid dissolved, increased with the volume of water; but that the concentration of the solution became less as the quantity

[1] Bulletins Nos. 114 and 118.
[2] Zeit. anorg. Chemie., *5* (1894), 87.
[3] Jour. Am. Chem. Soc., *26* (1904), 385.

FIG. 16. — LIMED AND UNLIMED POTATOES.

Both fertilized with muriate of potash and nitrate of soda. Showing after effect of *raw iron and aluminum phosphate*. Same amount of phosphoric acid as in Figs. 14–15 and 17–23.

FIG. 17. — LIMED AND UNLIMED POTATOES.

Both fertilized with muriate of potash and nitrate of soda. Showing after effect of "*ignited*" or "*roasted*" *iron and aluminum phosphate*. Same amount of phosphoric acid as in Figs. 14–16 and 18–23.

of the water was increased. A greater removal of phosphoric acid than of aluminum was shown, analogous to the case of the iron phosphate (Section 327). The same investigators found that aluminum phosphate behaves, toward solutions of potassium chlorid, in a similar manner as the calcium and iron phosphates; or in other words, that with an increase in the concentration of the chlorid the phosphoric acid in the solution became less. Similar results were noted also with potassium sulfate and with sodium nitrate. It appears therefore, that, like iron phosphate, the solubility of aluminum phosphate is affected much less by neutral salts than by acid or alkaline solutions.

326. Iron phosphate formed in soils. — The phosphate of iron is formed wherever dissolved phosphate is brought in contact in the soil with oxid of iron.

Phosphates of iron are often found associated with peat deposits, where through the reducing action of vegetable matter ferrous phosphate (the phosphate of the protoxid of iron) often occurs in large quantities.

Vivianite. — A ferrous phosphate, known as Vivianite ($Fe_3(PO_4)_2 \cdot H_2O$), occurs as a mineral, but it has not yet been proved to be common in soils, although this has been assumed by some writers.

327. The solubility of artificial ferric phosphate. — Experiments have been made by Lachowiez [1] with artificially prepared ferric phosphate which contained phosphoric acid considerably in excess of that (47.02 per cent) corresponding to the formula $FePO_4$. Such phosphate, after various treatments with hot or boiling water, yielded acid solutions containing but minute quantities of iron. The quantity of phosphoric acid in the residues after the

[1] Monatsh., *13* (1892), 357, cited from Cameron and Bell.

various treatments was lowered from 48.14 per cent to a minimum of 46.33 per cent. At the same time the per cent of Fe_2O_3 was raised from 48.97 (the formula $FePO_4$ requires 52.98 per cent) to a maximum of 61.98 per cent. After a considerable number of days a condition of equilibrium is reached between the solid and the solution. In order therefore, to effect a further removal of phosphoric acid fresh quantities of water are required. It has been inferred that it is possible, by a sufficient number of successive treatments with water, to remove all of the phosphoric acid, in which case only ferric hydroxid would remain. These results have been confirmed by Cameron and Hurst, who also experimented with a basic phosphate without however finding that it materially altered the character of the results. The presence of neutral salts, at least in certain concentrations, has no material effect upon the amount of phosphoric acid brought into solution, whereas salts having an alkaline reaction, as for example alkaline carbonates, increased the solvent power of the solution for the phosphoric acid of the ferric phosphate. The solubility was found to be especially marked in the case of the presence in solution of the carbonates and acetates of sodium and potassium. The same is also true of disodium phosphate, notwithstanding the probable formation in this case of a common ion.

Iron phosphates are soluble in alkali hydroxids and less readily in solutions of free mineral acids. Their solubility is also increased by the presence of salts which when hydrolized yield alkaline solutions.

It was found by Gerlach[1] that oxalic acid was a more effective solvent of artificial iron phosphate than citric acid and that this was even much superior to acetic acid. In

[1] Landw. Vers.-Sta., *46* (1895), 201.

the presence of free iron hydroxid, acetic acid had no appreciable solvent effect on the iron phosphate. Citric acid had far less effect under the same condition than otherwise, whereas the solvent action of oxalic acid was not influenced.

It was found by Cameron and Bell that there was a great and unexpected increase in acidity when iron phosphate was treated with solutions of certain neutral salts. This they attribute to selective absorption whereby the basic part unites with the solid residues leaving free acid in solution.

It is asserted that the presence of calcium carbonate may increase the solubility of iron phosphate, but in this particular calcium bicarbonate is far more effective.

CHAPTER XVI

MANUFACTURED PHOSPHATES AND STUDIES OF SOLUBILITIES

In recent years, owing to the great demand for phosphatic fertilizers and on account of the wide recognition of the necessity, for many purposes, of having them readily available, the ground raw and steamed bone have been very largely replaced by the artificially prepared phosphates.

328. The manufacture of basic slag meal. — Basic slag meal (not to be confused with non-phosphatic or but slightly phosphatic slags of ordinary blast furnaces) is a waste product of the manufacture of steel from iron phosphate by the modification of the Bessemer process developed by Thomas and Gilchrist of England. This consists in passing air through a mixture of molten iron phosphate and lime, in a large pear-shaped converter lined on the bottom and sides with a mixture of tar and lime, or magnesian lime. The tar is employed in order to make the lime adhere to the converter. A current of air is then forced through the mass until spectroscopic observations of the gases evolved show that the oxidation is complete. The slag formed by the union of the oxids of phosphorus and of silicon with lime, is then poured off by decanting the converter, after which the steel is drawn off below. After pulverization the slag meal is sold under the name of "basic cinder," "basic slag meal," or "Thomas phosphate powder."

In the earlier days of the manufacture of basic slag meal

it was found to vary greatly in its availability to plants, dependent upon the works from which the material came, and certain works in particular had the reputation of turning out a product having a very low efficiency as a fertilizer.

329. The influence of silica on the efficiency of basic slag. — It was finally discovered by Hoyermann of Hannover, Germany, and later fully established by the work of others, that this difference in availability was caused by variations in the amounts of silica which were present, and that frequently by the introduction of extra silica the efficiency of the resulting slag meal could be greatly increased. In consequence of this discovery there is now usually less difference than formerly in the availability of the European product, which at present constitutes the chief source of supply for the United States.

330. The range in composition of low and high grade basic slag. — There is produced in certain works in England a grade of basic slag meal with a very low content of phosphoric acid ranging usually from 12 to 14 per cent. There are on the other hand basic slag meals on the market containing from 25 to 28 per cent, but the grades more commonly brought into the United States usually contain from 16 to 19 per cent of phosphoric acid. It has been asserted that in some cases the percentage of phosphoric acid is raised by the introduction of tricalcium phosphate into the converter, with the result that the percentage of phosphoric acid is increased at the expense of the availability of the product. Certain Belgian exporters claim, nevertheless, that they can furnish slag meal, with the higher percentages of phosphoric acid, which has not been fortified in this manner.

331. The German methods of determining availability.

— The agricultural experiment stations of Europe busied themselves for some years in the attempt to find a laboratory method of treatment, capable of indicating essentially the same degree of availability of basic slag meal as was shown by experiments with plants. The method in use prior to 1899, consisted in extracting the material, under definite conditions, with an acid solution of ammonium citrate, but this was then replaced by a 2 per cent solution of citric acid, which is used in the present official German method. The purchase of basic slag meal on analysis, by this method, is advisable as an insurance against the introduction of ordinary tricalcium phosphate as an adulterant.

332. The degree of fineness. — The degree of fineness, and the total content of phosphoric acid, also furnish valuable criteria of the value of basic slag meal. In fact 80 per cent of it should readily pass through a sieve having 100 meshes to the linear inch.

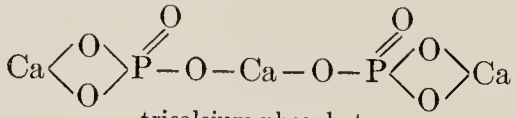
333. The chemical composition of basic slag. — In addition to phosphoric acid, basic slag usually contains calcium, magnesium, iron as ferrous and ferric oxids, calcium sulfid, and small quantities of oxids of manganese, vanadium, silicon, and sulfur. Such amounts of metallic iron as are present are usually separated by a magnet during the process of pulverization. The composition of the final product varies according to the composition of the lime, iron ore, and other materials added in the converter.

	Per Cent
Calcium oxid	40–60
Phosphorus pentoxid (P_2O_5)	10–20
Iron oxid	10–20
Silica	5–15
Manganese oxid	3–6
Magnesium oxid	2–6
Alumina	1–3

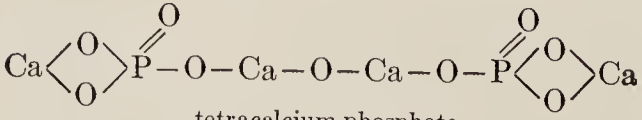
In general the composition of basic slag meal may be considered as ranging between the preceding limits.

The amount of free lime in basic slag meal is now less than formerly, owing to the greater amount of silica introduced into the converters. It usually ranges from 1 to 6 per cent, though the upper limit, recently determined by James Hendrick [1] in seven lots of basic slag with rather low phosphorus content which were sold in England, was only 3.08 per cent, as shown by the lime dissolved by long shaking with a 10 per cent sugar solution. The amount of lime capable of acting as a base, as determined by Hendrick in these slags, ranged from 13.6 to 28.3 per cent. The method used for this determination was distillation with ammonium sulfate and measurement of the equivalent, by the ammonia liberated. The introduction of the extra silica into the converter obviously increases the amount of calcium silicate present, and lessens the quantity of free lime.

334. As to the constitution of basic slag. — In case basic slag is cooled slowly, certain flat, square, plate crystals are formed, which upon analysis have been found to be tetracalcium phosphate, the structure of which as compared with tricalcium phosphate is shown below: —



tricalcium phosphate



tetracalcium phosphate

[1] Jour. Soc. Chem. Ind., *28*, 776.

The tetracalcium phosphate, if reacted on by weak acids, yields two molecules of calcium oxid to the acid and is transformed into dicalcium phosphate.[1]

It was long supposed that basic slag was strictly a tetracalcium phosphate, yet it was difficult to account for all of the lime on that supposition, even with due allowance for silica, sulfur, and for the lime which can be looked upon as " free " lime. Further doubt is thrown upon the basic slag being tetracalcium phosphate, by the fact that the flat crystals just mentioned are not found in slag which is rich in silica. The crystals usually formed under such circumstances are long hexagonal needles, pale green, or blue, in color, the presence of which would more readily account for the peculiar fracture of basic slag than the crystals of tetracalcium phosphate. These needle-shaped crystals have been shown by Stead to have the composition $(CaO)_5P_2O_5SiO_2$ which gives approximately 11 per cent of silica, 29 per cent of phosphoric acid, and 56 per cent of lime. When these crystals are subjected to the action of carbonic acid or dilute citric acid their solubility is found to accord far more nearly with that of basic slag meal, than the crystals of tetracalcium phosphate.

335. The practical use of basic slag meal. — Basic slag meal becomes especially available in the presence of considerable moisture and hence it usually acts well on clayey soils; it also improves their physical condition because of the presence of calcium oxid and calcium carbonate.

On peat or muck soils which are acid, basic slag meal has also been employed with splendid effect. Its use on sandy

[1] O. Förster, Zeit. f. angew. Chemie, *18*, 22 (1892); Jour. Soc. Chem. Ind., p. 460 (1892), cited from Hendrick.

soils is followed by excellent results except in case of extreme drought.

The ideal soils on which to use basic slag meal are acid uplands, for benefit to them not only results from the phosphoric acid, but also to a moderate degree from the free lime, and from the lime present as carbonate, silicate, and phosphate. This is by virtue of gradually lessening the soil acidity and consequently postponing the time when further liming will be necessary. A single or several repeated applications of basic slag meal will often bring in clover and create conditions favorable to the growth of timothy, barley, and other plants; whereas the use of acid phosphate or of double superphosphate may, under the same conditions, make the situation even slightly worse. If applied to acid pasture soils, basic slag meal aids in bringing in white clover, and thus materially adds to their value for grazing purposes. (See Fig. 18.)

336. Care in mixing basic slag with certain other materials. — Care must be taken not to mix basic slag meal with organic nitrogenous fertilizers in case they are to be stored before their application, especially if they absorb much moisture, for some loss of nitrogen as ammonia may result. It is equally important not to mix basic slag with acid phosphate or double superphosphate, for some of the lime will be neutralized thereby and hence lose much of its immediate corrective value. At the same time the lime would tend to cause the reversion of some of the soluble phosphoric acid, thus rendering the superphosphates less valuable, particularly for the purpose of top-dressing.

If basic slag is mixed with sulfate of ammonia, the free lime is sure to liberate some of the ammonia, and at the same time the lime will be transformed into land plaster or gypsum and hence lose its capacity for correcting the

FIG. 18. — LIMED AND UNLIMED POTATOES.

Both fertilized with muriate of potash and nitrate of soda. Showing after effect of *basic slag meal.* Same amount of phosphoric acid as in Figs. 13–17, and 19–23.

condition of acid soils. This reaction is shown by the following equation: —

$$(NH_4)_2SO_4 + CaO = CaSO_4 + NH_3 + H_2O$$

sulphate of ammonia — lime — gypsum — ammonia — water

For the reasons given above, basic slag meal should usually be applied to the soil by itself, though it can be mixed with nitrate of soda, nitrate of potash, and with the German potash salts without fear of loss or of the deterioration of any of the ingredients of the mixture.

337. Artificial basic slag meal. — On account of the popularity of basic slag meal and of the consequent increased demand for it, many attempts have been made to produce a similar product by a direct process of manufacture. To this end apatite and other phosphates have been fused with silica and lime whereby a strictly basic product is said to result, resembling in many respects genuine basic slag meal. Such products have been found to be soluble by the usual method of treatment with ammonium citrate, to the extent of 90 per cent of the phosphoric acid.

These products have been given various names, and they have also been sold as "artificial" basic slag.

338. Wiborgh phosphate. — This product has been prepared by fusing together feldspar, sodium carbonate, and phosphorite. It is also said to have been made without the introduction of the feldspar. The fusion is made at from 900° to 1000° C. The final product has been represented by the formula: $2\ Na_2O \cdot 10\ CaO \cdot 3\ P_2O_5$. The phosphoric acid is soluble to the extent of 21 to 27 per cent in a solution of ammonium citrate; and it has been found to compare favorably with superphosphate and basic slag meal. It is especially adapted to the peat soils of Sweden, where it has been chiefly used. It has

now been superseded by the Palmaer phosphate, which is produced more economically.

339. Wolter's phosphate. — Another artificial product quite similar to the preceding is made by fusing in a regenerative furnace 100 parts of powdered phosphorite, 70 parts of sodium sulfate, 20 parts of calcium carbonate, 22 parts of sand, and 6 to 7 parts of coke. The molten material is first run into water, and is at last finely pulverized. By this process the phosphoric acid is rendered almost wholly soluble in a 2 per cent citric acid solution. The phosphoric acid in this material has been found to be even more efficient than that in basic slag meal, and but slightly inferior to that in superphosphate.

340. Palmaer Phosphate. — In the Palmaer process a solution of sodium chlorate or of sodium perchlorate is electrolyzed. The acid anode solution is then made to react on the raw phosphate, which it readily dissolves. Thereupon some of the alkaline cathode solution is added, as a result of which dicalcium phosphate is precipitated as a fine crystalline powder. After this is separated by filtration, the remainder of the cathode solution is added to the filtrate, whereupon most of the lime in solution is separated as calcium hydrate. The remainder is then removed as carbonate by the introduction of carbonic acid. The electrolyte, thus regenerated by the process, again enters the electrolyzing apparatus.

The dicalcic phosphate thus produced contains 36 to 38 per cent of phosphoric acid, 95 per cent of which is soluble in a solution of ammonium citrate.

Experiments with this phosphate in Sweden, on sandy and on peat soils, have shown its direct and residuary effects to be on a par with those secured with superphosphate.

On peat soil the residuary effect of Palmaer phosphate has been found by Von Feilitzen to agree with acid phosphate but to be somewhat inferior to that secured with basic slag meal. By this process low-grade apatites can be utilized.

341. Other artificial phosphates. — By heating a mixture consisting of equal parts of 55 per cent phosphoric acid and either ammonium sulfate or potassium sulfate, at 80° C. there results a pulverulent product. The following illustrates the course of the reaction with potassium sulfate: —

$$K_2SO_4 + H_3PO_4 = KHSO_4 + KH_2PO_4.$$

This product contains 24 per cent of phosphoric acid, and 27 per cent of potash. The corresponding product made by substituting ammonium sulfate for the potassium sulfate, contains 25 per cent of phosphoric acid and 10.5 per cent of nitrogen. A corresponding sodium salt cannot be prepared in this manner. On account of the acid character of this material, due to its containing 30 per cent of sulfuric acid, it may be mixed to advantage with basic slag meal, at least in so far as concerns the availability of the phosphoric acid. It is also especially applicable on calcareous soils.

From low-grade calcium phosphate. — Another artificial product is prepared on a similar principle by the introduction of a low-grade calcium phosphate, too rich in calcium carbonate for profitable superphosphate manufacture. By suitable processes of evaporation, filtration, and desiccation an excess of sulfuric acid is avoided and there is produced a sulfo-phosphate containing 38 to 40 per cent of phosphoric acid, which is chiefly soluble. It also contains 31 to 33 per cent of

potash and small quantities of sulfuric acid, lime, and other substances.

From aluminum phosphate. — Redonda phosphate and other similar aluminum phosphates can be utilized, in a similar way, to make sulfo-phosphates of ammonia and aluminum sulfate, by fusing the phosphate with ammonium disulfate for from two to three hours. The reaction is as follows: — $2\,AlPO_4 + (NH_4)\,HSO_4 + H_2SO_4 = Al_2(SO_4)_3 + 2\,(NH_4)HSO_4 \cdot (NH_4)H_2PO_4$). Practical difficulty arises in this treatment, due to the presence of aluminum sulfate, but this may be obviated by adding an equivalent amount of ammonium disulfate, whereupon a product is obtained which remains dry. The reaction is then as follows: — $AlPO_4 + 3\,(NH_4)HSO_4 = Al(NH_4)(SO_4)_2 + (NH_4)HSO_4 \cdot (NH_4)H_2PO_4$.

By the use of bisulfate. — A so-called " bisulfate-superphosphate " has been prepared by treating Algerian phosphate with bisulfate refuse from nitric acid works. If properly managed, a dry product results which contains from 7 to 8 per cent of soluble phosphoric acid.

342. The preparation of superphosphates. — In order to secure a greater efficiency of phosphoric acid than is possible when it is in the state of tricalcium phosphate, the latter is treated with sulfuric acid. In this process two-thirds of the lime combines with sulfuric acid to form land plaster, or gypsum, which remains in the mixture with the monocalcium phosphate (soluble phosphoric acid) which is produced. The resulting mixture is called " superphosphate." If made from spent bone-black, it is given the name of " dissolved bone-black"; if from bone, " dissolved bone "; and if from mineral tricalcium phosphate, either " plain superphosphate " or " acid phosphate." The reaction is shown by the following

equation: —

$$\underset{\text{tricalcium phosphate}}{Ca_3(PO_4)_2} + 2\,\underset{\text{sulfuric acid}}{H_2SO_4} = 2\,\underset{\text{calcium sulfate}}{CaSO_4} + \underset{\text{monocalcium phosphate}}{CaH_4(PO_4)_2}.$$

In the practical application of the process, small quantities of free phosphoric acid, dicalcium phosphate, and tricalcium phosphate are present in the product.

343. Treatment of bone with small amounts of sulfuric acid. — A few years ago much interest was awakened by a proposition to use only about half the usual amount of sulfuric acid, in the treatment of bone. By this means the cost of the treatment was greatly lessened, and yet the material produced was claimed to possess a very high degree of manurial efficiency. Such a product, because of its slight solubility, would, however, not be fully satisfactory for the top-dressing of either grass lands or grain crops. By this process only one-third of the lime would be removed from the tricalcium phosphate, as suggested below: —

$$\underset{\text{tricalcium phosphate}}{Ca_3(PO_4)_2} + \underset{\text{sulfuric acid}}{H_2SO_4} = \underset{\text{calcium sulfate}}{CaSO_4} + 2\,\underset{\text{dicalcium phosphate}}{CaHPO_4}.$$

344. Free phosphoric acid in superphosphate. — If more sulfuric acid is used than is customary for the production of monocalcium phosphate, considerable free phosphoric acid is formed; and by employing enough sulfuric acid to replace all of the lime, the following would be the course of the reaction: —

$$\underset{\text{tricalcium phosphate}}{Ca_3(PO_4)_2} + 3\,\underset{\text{sulfuric acid}}{H_2SO_4} = 3\,\underset{\text{calcium sulfate}}{CaSO_4} + 2\,\underset{\text{phosphoric acid}}{H_3PO_4}.$$

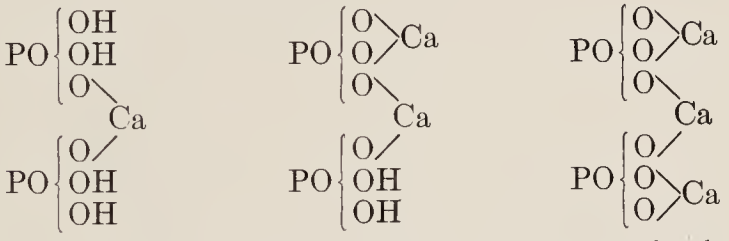
345. The strictly chemical use of the term "phosphoric acid." — The name phosphoric acid is properly applied

only to the hydrated compound H_3PO_4, though it is commonly used in agricultural literature in referring to the phosphorus pentoxid (P_2O_5).

346. The relationship of the various phosphates.— The relationship of the tribasic orthophosphoric acid, with its three hydrogen atoms replaceable by a metal, is shown below: —

orthophosphoric acid | monometallic orthophosphate | dimetallic orthophosphate | trimetallic orthophosphate

The union of calcium, a divalent element, with orthophosphoric acid is illustrated as follows: —



monocalcium phosphate or acid phosphate of lime $CaH_4(PO_4)_2$

dicalcium phosphate or monacid phosphate of lime $2\ CaHPO_4$

tricalcium phosphate or neutral phosphate of lime $Ca_3(PO_4)_2$

347. Care in the manufacture of superphosphate.— In the manufacture of superphosphate the composition of the raw phosphate must be determined in advance, in order that the right quantity of sulfuric acid of the proper strength may be employed. If, for example, calcium fluorid or calcium carbonate is present, allowance must be made for them so that sufficient acid will remain to react

properly upon the phosphate. On the other hand, manufacturers avoid, in so far as possible, the formation of free phosphoric acid, for the reason that the mass is then likely to be moist, to be more difficult to handle, and to be much more destructive to the bags used in its shipment.

348. The practical process of making superphosphate.— Chamber acid, because of its cheapness, is usually employed instead of purer grades of sulfuric acid. This has a specific gravity of 1.5 to 1.6. The acid and the raw ground phosphate are introduced into a mixer, and the whole mass is then passed into a "den." There the chief reaction follows in the course of a few hours, though the material is usually allowed to react for some days. During this time a very high temperature is developed, often exceeding 100° C., which is highly favorable to the decomposition of the remaining tricalcium phosphate. The gypsum produced, combines with the excess of moisture; and after a short time the material dries out enough so that it can be readily broken up and brought into a friable and fit condition for use. At present, in certain works, the gases coming from the dens are condensed, the liquors concentrated in lead pipes or chambers, and the compounds of fluorin prepared therefrom are used in enameling porcelain and for other purposes.

349. Double superphosphate. — An unusually high grade of superphosphate found on the market in this country and in Europe is the "double" superphosphate. This is made by treatment of low-grade phosphates with an excess of dilute sulfuric acid. By use of filter presses the gypsum and other insoluble impurities are largely separated from the remaining liquid mixture, which consists of sulfuric acid, monocalcium phosphate, and free phosphoric acid. This liquid is then highly concentrated, by evapora-

tion, until it is sufficiently strong for use in treating the highest grades of rock phosphates, or until it is of proper strength to be used as a dilutant of ordinary sulfuric acid, employed for that purpose. The reaction of the free phosphoric acid of the solution upon the tricalcium phosphate is represented by the following equation : —

$$\underset{\text{tricalcium phosphate}}{Ca_3(PO_4)_2} + 4\ \underset{\text{phosphoric acid}}{H_3PO_4} = 3\ \underset{\text{double superphosphate (monocalcium phosphate)}}{CaH_4(PO_4)_2}.$$

By the process described above, the content of monocalcium phosphate may be raised so that a product containing from 40 to 45 per cent of soluble phosphoric acid is produced. It contains, however, free phosphoric acid in excess and is on this account difficult to dry. It may also prove slightly injurious for a few days on a very acid soil, if used with plants which are especially sensitive to acidic conditions.

It is possible by leaching ordinary superphosphate with water, and by evaporation of the solution, to obtain a material with as high as 60 per cent of soluble phosphoric acid.

High-grade superphosphates are prepared in Europe as a by-product from the manufacture of gelatine.

The direct manufacture of these high-grade phosphates is economical only where fuel is cheap and where sulfuric acid and low-grade phosphates are available at very low cost; or where the material must be transported for long distances, as may yet be the case in the United States when the phosphate beds of Florida and Tennessee are exhausted and those of the far West must be drawn upon to supply the needs of the East.

These high-grade phosphates are often of material

service to the fertilizer manufacturer in the preparation of some of the higher grades of mixed fertilizers, for by their use lower grades of potassium salts or of nitrogenous materials may be employed than would otherwise be possible. (See Fig. 19.)

350. Dissolved bone. — Raw bone is now seldom treated with sulfuric acid, for the purpose of manufacturing dissolved bone, owing to the fact that it yields a sticky, gelatinous mass which it is difficult to handle.

By steaming, bone becomes friable, and it may then be treated with sulfuric acid without difficulty. Owing to the removal of much of the fat and organic matter by this process, the mass dries out within a few hours after acidulation so that it can either be easily ground and utilized directly as a fertilizer, or it may be introduced into mixtures of other fertilizer materials.

Dissolved steamed bone necessarily varies somewhat in composition according to the character of the bone used in its manufacture. It may be safe to say that it usually contains from 1 to 3 per cent of nitrogen. It also contains from 15 to 18 per cent of phosphoric acid, the major portion of which is soluble in water. (See Fig. 20.)

351. Dissolved bone-black. — The waste bone-black from sugar refineries, and the highly carbonized bone residues from annealing processes, yield, upon treatment with sulfuric acid, a superphosphate similar to that from bone, excepting for the fact that it contains little or no nitrogen.

Towards the close of the preceding century acid phosphate began to gradually replace dissolved bone-black, but still the prejudice of many farmers was so strong against any fertilizer made from rock that acid phosphate was dyed black, in some cases, in order that it

FIG. 19. — LIMED AND UNLIMED POTATOES.

Both fertilized with muriate of potash and nitrate of soda. Showing after effects of *acid phosphate*. Same amount of phosphoric acid as in Figs. 14–18 and 20–23.

FIG. 20. — LIMED AND UNLIMED POTATOES.

Both fertilized with muriate of potash and nitrate of soda. Showing after effects of *dissolved bone*. Same amount of phosphoric acid as in Figs. 14–19 and 21–23.

might be sold for dissolved bone-black. Dyed acid phosphate was also introduced into some mixed fertilizers, which had been compounded previously by the use of dissolved bone-black; but as farmers came to understand that dark or black fertilizers were not necessarily better than others, the tendency to resort to such measures ceased. (See Fig. 21.)

352. Laboratory studies on the solubility of phosphates. — The recent exploitation of raw rock phosphate, as a fertilizer, makes a consideration of the action of certain solvents upon the various phosphates of special interest. It must not, however, be forgotten that in the soil many individual factors, including living organisms, are at work; and many of the chemical and physical conditions are also entirely different from those of the laboratory. Many of the phosphates studied in the laboratory are artificial products. They are in consequence not of the same physical character as certain of the phosphates with which the farmer has to deal. For these reasons great care should be taken in attempting to apply all such laboratory findings to the conditions practically met with in the field.

With this precautionary introduction it may be well to consider certain laboratory observations, which may have a direct, or, more frequently, indirect, bearing upon the practical utilization of phosphates.

353. The action of water on monocalcium phosphate. — As concerns the action of water upon monocalcium phosphate there exist widely divergent statements. These differences are believed to be due to the fact that some of the monocalcium phosphate employed by the different experimenters contained a little free phosphoric acid, which increased its solubility; furthermore, owing

FIG. 21. — LIMED AND UNLIMED POTATOES.

Both fertilized with muriate of potash and nitrate of soda. Showing after effects of *dissolved bone-black*. Same amount of phosphoric acid as in Figs. 14–20 and 22–23.

to the hygroscopic nature of the free acid, and to the water therefore absorbed, the amount of actual monocalcium phosphate employed may sometimes have been less than was supposed.

From recent investigations it also appears that upon the addition of water to monocalcium phosphate a certain amount of hydrated dicalcium phosphate ($CAHPO_4 \cdot 2\ H_2O$) is formed, and at still higher temperatures even the anhydrous salt ($CaHPO_4$), which, unlike the hydrated salt, is insoluble in citric acid. At the same time the resulting solution contains a higher ratio of phosphoric acid to lime, than the monocalcium phosphate. This is indicated partially by the equation which follows: —

$$CaH_4(PO_4)_2 \cdot H_2O + H_2O = CaHPO_4 + 2\ H_2O + H_3PO_4.$$

The free phosphoric acid therefore carries with it into the solution some dicalcium phosphate. The addition of more water results in changing relatively more of the monocalcium phosphate into free phosphoric acid and dicalcium phosphate, whereas the addition of phosphoric acid to the solution renders more of the dicalcium phosphate soluble.

Experiments by Joly [1] have shown that the addition of monocalcium phosphate to a given amount of water resulted, up to certain limits, in a marked increase in the free phosphoric acid in solution; but at the temperature at which he worked, the addition of an excess of monocalcium phosphate beyond 65 grams to 100 grams of water, resulted in no further decomposition of the salt nor in further change in the composition of the solution.

Under this last condition there are, according to Cam-

[1] Compt. rend., *97* (1883), 1480.

eron, two solid phases, viz. monocalcium and dicalcium phosphate.

It has been shown by Cameron and Seidell [1] at a temperature of 25° C., that when both the monocalcium phosphate and dicalcium phosphate are present as solid phases, the amount of "free" phosphoric acid (P_2O_5) was 120 grams, per liter of solution.

354. The action of water on dicalcium phosphate. — When water is added to dicalcium phosphate, there is produced on the one hand a solution, and on the other an amorphous solid containing a greater ratio of lime to phosphoric acid than is present in the dicalcium phosphate. This solid was formerly regarded as tricalcium phosphate.

It has been shown by Millot and confirmed by Viard [2] that when dicalcium phosphate is acted upon by boiling water, free phosphoric acid and some lime go into solution, whereas the solid phase is composed of amorphous tricalcium phosphate and anhydrous dicalcium phosphate. It was supposed by certain investigators, however, that the solid was tricalcium phosphate and that monocalcium phosphate resulted, which passed into solution. Definite formulas have been ascribed by some investigators to the solid compounds resulting from treating dicalcium phosphate with water, under the assumption that they were dealing with a distinct compound rather than with a mixture of two solid phases, or with a series of solid solutions. That the latter was probably the case has been shown by Rindell, who insured final conditions of equilibrium by determining at intervals the electrical conductivity of the solutions with which he worked.

[1] Jour. Am. Chem. Soc., *27* (1905), 1503.
[2] Compt. rend., *127* (1898), 178.

It has been shown recently by Buch [1] that after subjecting dicalcium phosphate to fifty-three successive leachings with water, it had been transformed completely into tricalcium phosphate; and he suggests the possibility of carrying the transformation still further, in view of the basic compounds of phosphoric acid which are known to exist in nature.

The solubility increased by carbonic acid. — The solubility of dicalcium phosphate has been shown by Dusart and Pelouze [2] to be more than two and one-fourth times as great in water saturated with carbon dioxid as in pure water; and Cameron and Seidell found that solid gypsum increased the solvent action of water saturated with carbon dioxid.

355. The action of water on tricalcium phosphate. — In connection with a study of tricalcium phosphate, it was found unstable when brought in direct contact with water, and it yielded a solution having a higher ratio of phosphoric acid to lime than was possessed by the original phosphate. At the same time a phosphate with increasing basicity is produced which, according to Cameron and Bell,[3] also "becomes decreasingly soluble on repeated treatment with water." According to the same authorities the soil water, containing both mineral and organic matter, doubtless exerts a much greater solvent action on the phosphoric acid of the tricalcium phosphate than is exerted by pure water.

If the first work is right, it appears to offer a partial explanation of the long-continued after-effects which follow the application of superphosphates to soils, for by the

[1] Zeits. anorg. Chem., *52* (1907), 325.
[2] Compt. rend., *66* (1868), 1327; cited from Cameron and Bell.
[3] Bul. 41, Bureau of Soils, U. S. Dept. of Agr. (1907).

reaction of the monocalcium phosphate with such basic phosphates as may be present therein, the basicity of the latter should become less, and much of the phosphoric acid would consequently remain, for a considerable period, much more readily soluble than that present at the outset in the original basic phosphate.

It appears from what has preceded that what is generally spoken of as tricalcium phosphate cannot be considered as a definite chemical compound, in all cases, but rather, in most instances, as one of a series of solid solutions of lime and phosphoric acid.

The solubility increased by carbonic acid. — It has been shown by many experimenters that tricalcium phosphate is more soluble in water containing carbon dioxid than it is in pure water.

A number of determinations were made by Schloesing[1] of the solubility of a phosphate which, by analysis, was shown to be very close to a tricalcium phosphate. The results secured by treating a gram of the phosphate for a day at 16° to 20° C. with 1250 c.c. of solvent, were found to be as shown on the following page.

The table shows the great influence of carbon dioxid on the solubility of such phosphate, and the low solubility of the phosphoric acid, in all cases, in the presence of large amounts of calcium carbonate. This action of calcium carbonate and of other calcium salts in depressing the solubility of tricalcium phosphate, even in the presence of carbon dioxid, has been suggested as being due possibly to the formation of a common ion (Ca) which lessens the quantity of phosphoric acid which passes into solution. On this basis potassium chlorid would be expected to have a solvent action upon tricalcium phosphate, and this has

[1] Compt. rend., *131* (1900), 149.

Solvent	P_2O_5 per Liter. Milligrams	CaO per Liter. Milligrams
Water	0.74	
1200 c.c. distilled water and 50 c.c. water saturated with CO_2	6.90	
1000 c.c. distilled water and 250 c.c. water saturated with CO_2	48.50	
1250 c.c. water saturated with CO_2	91.90	
Water containing 174 mmg. of $CaCO_3$ and 82 mmg. of CO_2 per liter	0.38	100
Water containing 290 mmg. of $CaCO_3$ and 171 mmg. of CO_2 per liter	1.10	162
Water containing 389 mmg. of $CaCO_3$ and 270 mmg. of CO_2 per liter	0.80	219
Water containing 488 mmg. of $CaCO_3$ and 415 mmg. of CO_2 per liter	1.77	273
Water containing 558 mmg. of $CaCO_3$ and 541 mmg. of CO_2 per liter	1.30	313

been shown by Cameron and Hurst to be the case; though they found that it also had a decomposing action, as would reasonably be expected.

The solubility and decomposability increased by certain substances. — Sodium nitrate, sodium chlorid, and solutions of gelatine, sugar, and albumin have all been shown to have a solvent, and in some cases also a decomposing action on tricalcium phosphate.

356. Determination of "soluble" phosphoric acid. — In the analysis of commercial fertilizers the first step in the determination of phosphoric acid is to place a weighed portion of the material on a filter paper, and then to leach it with water. By this operation practically all of the monocalcium phosphate ($CaH_4(PO_4)_2$) is dissolved, and other changes in associated phosphates, as suggested previously, occur to a slight extent. The quantity of the

dissolved "phosphoric acid" is determined and reported as "soluble" phosphoric acid (phosphorus pentoxid P_2O_5).

357. Advantages of soluble phosphoric acid. — One advantage of monocalcium phosphate over other phosphates is due to the fact that it is readily dissolved by water; and if applied as a top-dressing it is easily carried into the soil. If incorporated with the soil at the outset, it also becomes more generally distributed, as the result of subsequent rainfalls, than would be the case if the phosphate were introduced in an insoluble state.

358. The reversion of monocalcium phosphate. — It is well known that the monocalcium phosphate after entering the soil, passes at once, or very quickly, in the presence of considerable moisture, into less soluble combinations. Indeed solutions of monocalcium phosphate, if simply heated, or if allowed to stand for some time at ordinary temperatures, break up into dicalcium phosphate and phosphoric acid as follows: —

$$\underset{\text{monocalcium phosphate}}{CaH_4(PO_4)_2} = \underset{\text{dicalcium phosphate}}{CaHPO_4} + \underset{\text{phosphoric acid}}{H_3PO_4}.$$

This change takes place to some extent even in the drying of superphosphate in the factory. This is especially true of superphosphate made from Florida phosphates, and from such other phosphates as yield a rather moist product.

If the soil contains calcium carbonate, a considerable part of the monocalcium phosphate is supposed to react with it to produce essentially tricalcium phosphate, as follows: —

$$\underset{\text{monocalcium phosphate}}{CaH_4(PO_4)_2} + 2\,\underset{\text{calcium carbonate}}{CaCO_3} = \underset{\text{tricalcium phosphate}}{Ca_3(PO_4)_2} + \underset{\text{water}}{H_2O}.$$

It is supposedly for this reason, in part, that on acid soils the application of lime coincidently with, or prior to, the application of monocalcium phosphate, is desirable; for otherwise far more of the monocalcium phosphate would presumably react with iron and aluminum oxids and hence become subsequently less available to plants than the finely divided and newly formed tricalcium phosphate.

359. Liming after reversion with iron and aluminum oxids. — In case superphosphates have been applied sucessively to soils rich in iron and aluminum oxids and poor in calcium carbonate, the proper course, if one wishes to render the phosphoric acid available, is to lime the land quite heavily; for, as has been pointed out by Dehérain in France, such a procedure is followed by the transformation of much of the unavailable phosphoric acid into calcium combinations which can be more readily utilized by plants. Similar remarkable effects of lime in rendering the phosphorus compounds of the soil available to plants, or at least in rendering the application of phosphates no longer necessary, have been observed at the experiment station of the Rhode Island State College in connection with a soil which had received no phosphates for at least a dozen years. Similar marked benefit from liming also resulted on soil to which roasted aluminum phosphate (containing some iron phosphate) had been applied. Indeed, this benefit from liming in the latter case continued for several years after the last application of the lime and of the aluminum phosphate was made. A similar effect of applying lime was in some cases either entirely lacking,

or it was far less striking, in connection with the use of the unroasted aluminum phosphate.

360. The determination of "reverted" phosphoric acid. — After a sample of fertilizer has been leached with water, in the regular course of analysis, it is again extracted under definite conditions by digestion for one-half hour with a neutral solution of ammonium citrate. This treatment readily brings into solution phosphoric acid present as dicalcium phosphate ($CaHPO_4$), regardless of whether it was formed by the reversion of monocalcium phosphate or otherwise.

361. "Reverted" phosphoric acid not all from dicalcium phosphate. — In addition to dicalcium phosphate there is also dissolved by this treatment about one-half of the phosphoric acid which is present in steamed bone tankage, and a considerably less proportion of that in steamed bone. The ammonium citrate solution also dissolves to a great extent the phosphoric acid present in roasted iron and aluminum phosphates.

Since the term "reverted" is applied to all of the phosphoric acid removed by the extraction with ammonium citrate solution, it is evident that the so-called reverted phosphoric acid may be derived from dicalcium phosphate, tricalcium phosphate, and even from iron and aluminum phosphates. It is obvious, therefore, that its value to the farmer is likely to be variable, and conditioned not only upon its source, but in some cases even upon whether it is used on soils which are acid or upon those which are well supplied with carbonate of lime.

362. The term "available" phosphoric acid. — Available phosphoric acid is the term applied to the sum of the soluble and reverted phosphoric acid, determined as just described. It is therefore a trade term, rather

than one always strictly indicative of its agricultural value.

363. Insoluble phosphoric acid. — The phosphoric acid remaining undissolved after the successive extractions with water and ammonium citrate solution is finally determined and designated "insoluble" phosphoric acid. If such phosphoric acid is present in bone and in bone tankage, it will have a materially higher crop-producing value than if it is present in mineral tricalcium phosphate. If in this latter form, it will likewise be more readily available to plants than if present in powdered apatite or in the unroasted phosphates of iron and aluminum. It is obvious, therefore, that the mere analytical statement may fail, in certain particulars, to give complete information concerning the probable fertilizing value of the insoluble, as well as of the reverted, phosphoric acid. As concerns the soluble phosphoric acid, on the contrary, it is equally valuable, regardless of the source from which it may have been derived.

364. The reversion of monocalcium phosphate. — In addition to the reversion of monocalcium phosphate to dicalcium phosphate, and finally to tricalcium phosphate, when brought together with calcium carbonate, monocalcium phosphate may react upon tricalcium phosphate, in the presence of moisture, in such a way that, for many months after a fertilizer is mixed, the soluble and the insoluble phosphoric acid become gradually less and the reverted phosphoric acid increases correspondingly. This reaction may be expressed as follows: —

$$\underset{\text{tricalcium phosphate}}{Ca_3(PO_4)_2} + \underset{\text{monocalcium phosphate}}{CaH_4(PO_4)_2} = 4\ \underset{\text{dicalcium phosphate}}{CaHPO_4}.$$

365. Reversion often beneficial in some respects. — Such a reaction, though beneficial from the standpoint of the availability of the phosphoric acid present originally in the insoluble tricalcium phosphate, lessens the value, at least for top-dressing, of the phosphoric acid present at the outset in the "soluble" state. Owing to the considerable amount of water involved in the formation of the hydrous salt which s produced ($CaHPO_4 \cdot 2\ H_2O$), the rate of the reaction in fertilizers in storage is determined in part by the rate at which water can be absorbed from the air, although in the soil this change would be very rapid.

366. Reversion with iron and aluminum oxids serious. — The most serious form of reversion which may result in a superphosphate in the soil, is that which takes place when monocalcium phosphate reacts upon iron and aluminum oxids or upon sulfates of these elements. The first of these reactions may be suggested by the following:—

$$\underset{\text{ferric hydrate}}{2\ Fe_2(OH)_6} + \underset{\text{monocalcium phosphate}}{3\ CaH_4(PO_4)_2} = \underset{\text{ferric phosphate}}{2\ Fe_2(PO_4)_2} + \underset{\text{tricalcium phosphate}}{Ca_3(PO_4)_2} + \underset{\text{water}}{12\ H_2O}.$$

The tricalcium phosphate produced in this case can react upon further quantities of monocalcium phosphate to cause additional reversion.

It is well understood that the presence of iron oxid, in excess of 2 per cent, in phosphates intended for superphosphate manufacture, is objectionable, and that above 4 per cent is prohibitive. This is due to the fact that the oxid is dissolved by the sulfuric acid, and thus the way is paved for the more rapid subsequent reversion of the phosphoric acid. This is a most serious form of reversion because of the low availability of the iron phos-

phate produced, especially under unfavorable soil conditions.

The reaction just referred to is a reversible one, as indicated below: —

$$3\ FePO_4 + 3\ H_2SO_4 \rightleftarrows (FePO_4 \cdot 2\ H_3PO_4) + Fe_2(SO_4)_3.$$

However, in the presence of an excess of sulfuric acid, it proceeds as follows: —

$$2\ FePO_4 + 3\ H_2SO_4 \rightleftarrows 2\ H_3PO_4 + Fe_2(SO_4)_3.$$

The reaction of such compounds with monocalcium phosphate is shown by the following: —

$$Fe_2(SO_4)_3 + CaH_4(PO_4)_2 = 2\ FePO_4 + CaSO_4 + 2\ H_2SO_4.$$

Notwithstanding that this reaction is probably never complete, a great amount of insoluble ferric phosphate is nevertheless formed. The sulfuric acid set free might then unite with more iron, and thus the process could be repeated until equilibrium is finally established.

Reactions are possible with aluminum compounds, similar to those described above for ferric oxid and for ferric sulfate.

In case ferrous oxid were present, instead of the ferric oxid, a possible reaction has been suggested as follows: —

$$\underset{\substack{\text{ferrous}\\\text{sulfate}}}{4\ FeSO_4} + \underset{\substack{\text{oxy-}\\\text{gen}}}{2O} + \underset{\substack{\text{monocalcium}\\\text{phosphate}}}{CaH_4(PO_4)_2} + \underset{\substack{\text{tricalcium}\\\text{phosphate}}}{3\ Ca(PO_4)_2}$$

$$= \underset{\substack{\text{ferric}\\\text{phosphate}}}{4\ FePO_4} + \underset{\substack{\text{calcium}\\\text{sulfate}}}{4\ CaSO_4} + \underset{\text{water}}{2\ H_2O}$$

According to Schucht, however, who demonstrated the matter experimentally, the reaction takes the following course: $CaH_4(PO_4)_2 \cdot H_2O + Fe_2(SO_4)_3 + 5\ H_2O = FePO_4 \cdot 2\ H_2O + CaSO_4 \cdot 2\ H_2O + 2\ H_2SO_4$; then, $H_2SO_4 + CaH_4(PO_4)_2 \cdot H_2O = CaSO_4 \cdot 2\ H_2O + 2\ H_3PO_4$; and,

finally, $2\,(FePO_4 \cdot 2\,H_2O) + 4\,H_3PO_4 = 2\,(FePO_4 \cdot 2\,H_3PO_4) + 4\,H_2O$. In fact, the hydrated iron phosphate may, in the superphosphate, become wholly insoluble again, as shown below: —

$$FePO_4 \cdot 2\,H_2O + CaSO_4 = CaSO_4 \cdot 2\,H_2O + FePO_4.$$

It is for the foregoing reasons that the Redonda and other iron and aluminum phosphates cannot be utilized for superphosphate manufacture, and hence are roasted, or subjected to certain other chemical treatment, as a means of increasing their availability.

367. Reversion as affected by pyrite. — The presence in phosphates of small amounts of pyrite (FeS_2) and of silicates of iron and aluminum is sometimes unobjectionable from the standpoint of the superphosphate manufacturer, for the reason that they are usually but partly soluble in sulfuric acid and do not react with monocalcium phosphate. Nevertheless, the solvent action of these substances does not always hinge upon sulfuric acid only, for the hydrofluoric acid liberated from the calcium fluorid, often present in superphosphates, readily decomposes silicates. Under certain conditions aluminum silicate in considerable amounts may therefore eventually cause reversion of the phosphoric acid.

368. The fixation of superphosphates in soils rapid. — Many experiments have been conducted with soils, embracing those which are highly calcareous, sandy, and clayey, also with and without admixtures of precipitated calcium carbonate, marl, oxids of iron and alumina, in order to ascertain the rapidity of the fixation of soluble phosphoric acid. In many of these laboratory experiments, as, for example, in one by Schroeder in which two parts by weight of superphosphates were used with eight

parts of loam, the proportions between superphosphate and soil were entirely unlike those existing in the field, for in actual practice only from 200 to 1200 pounds of superphosphate are usually applied per acre, representing a depth of from six to ten inches of soil. Notwithstanding, therefore, that in the former case only a trifle over half of the phosphoric acid was fixed at the end of twenty days, the usual application in the field might, under favorable conditions of rainfall, have been fixed in a single day. In fact, a great preponderance of evidence supports the idea that very rapid fixation of soluble phosphoric acid takes place under the usual conditions of farm practice, provided the rainfall is sufficient to largely dissolve and distribute the monocalcium phosphate; and that losses by leaching are small. In times of drought, however, particles of superphosphate which have lain for a considerable period in the soil have been found to still contain soluble phosphoric acid.

369. The fixation of phosphates confined chiefly to the surface soil. — Upon examining the soil of the Broadbalk wheat field at the Rothamsted experiment station in England, Dyer found that notwithstanding the fifty annual applications of 350 pounds per acre of high-grade superphosphate, the subsoil from a depth of nine inches downward contained practically no more phosphoric acid removable by a 1 per cent citric acid solution than where none had been applied. Nevertheless, the upper nine inches of soil showed that it had been enormously enriched by phosphoric acid which the citric acid solution was capable of extracting. It must be evident in this case that if the fixation had not been very rapid, much of the phosphoric acid must have been washed into and fixed by the subsoil.

The analysis of the drainage waters at Rothamsted has shown but a trifling loss of phosphoric acid, which further supports the foregoing conclusion.

370. The availability of fixed phosphates may still be high. — It has been found at the Rothamsted station that five or six successive extractions of the soil with the citric acid solution bring it to a state where subsequent extractions fail to yield materially more than was removable from the original soil phosphates. The sum of the amounts of phosphoric acid removed in the first five extractions, added to that taken out by the crops of the fifty years, also agrees very closely with the quantity added during the interval, in superphosphates. In this particular case the efficiency of the stored-up phosphate was doubtless greatly enhanced by the presence in the soil, during the interval, of considerable quantities of carbonate of lime. Under this condition less phosphoric acid probably entered into combination with iron and alumina than would otherwise have been the case. See Fig. 22.

371. Injury from applications of superphosphate rare. — If superphosphates are applied a short time before planting, there is no likelihood of their causing injury to the crops. A striking instance of injury to oats, when applied just before seeding, was noticed upon an unlimed acid soil at the experiment station of the Rhode Island State College, in the case of double superphosphate, although it was not observable with any of the other superphosphates which were used. This ill effect, however, which was indicated by the unhealthy appearance and blanching of the tips of the leaves, finally disappeared within an interval of only a few days, probably after the initial acidity had been reduced, by the soil reactions, below the critical point for that particular plant.

Limed Unlimed

Large Small Large Small

FIG. 22. — LIMED AND UNLIMED POTATOES.

Both fertilized with muriate of potash and nitrate of soda. Showing after effects of *double superphosphate.* Same amount of phosphoric acid as in Figs. 14–21 and 23.

Limed Unlimed

Large Small Large Small

FIG. 23. — LIMED AND UNLIMED POTATOES.

Both fertilized with muriate of potash and nitrate of soda. Showing effects of *no phosphate.* Same amount of phosphoric acid as in Figs. 14–22.

372. Soils on which superphosphates may give poor results. — It has been found on the acid peat soils of Germany (Hochmoor) that the *first* application of acid phosphate often has little effect and that the use of dicalcium phosphate, bone, basic slag meal, or even of certain unacidulated mineral phosphates is followed by better results. On such soils, as well as on those which are light and sandy and more or less acid, the use of acid phosphate is not likely to be followed by the best possible results, unless they have first been limed.

373. Superphosphates have a flocculating action on soils. — In experiments by Sachsse and Becker [1] it was shown that superphosphate has a greater flocculating effect upon clayey particles of soils than either gypsum or lime. It should therefore improve their tilth and their ability to hold and to deliver water properly to the plant. Superphosphate is recognized as improving, in this particular, such soils as have been made alkaline by long use of nitrate of soda.

374. Various soil conditions affecting the choice of phosphate to be used. — It has often been reported that on the highly calcareous soils of Norfolk, England, where fine bone meal was of little value, superphosphates were found to act splendidly on the turnip crop; for they not only encouraged immediate and vigorous growth, but pushed the plants along so fast that they very largely escaped injury from the turnip fly.

Acid soils of every kind are not as a rule ideally adapted to superphosphates unless they have first received applications of wood-ashes, or lime in some suitable form.

On all ordinary soils, superphosphates are especially

[1] Die landw. Vers.-Sta., *43* (1894), 22. Cited from E. S. R., *5*, 696.

effective, and, contrary to a somewhat common idea, the after-effects from their use are long continued.

Notwithstanding that superphosphate acts well on certain highly calcareous soils, Petermann recommends especially for them the dicalcium phosphate, which is not only easily dissolved by carbonic acid, but is also readily drawn upon by plants, by virtue of the direct action of their roots upon the phosphate.

375. Crops and conditions for which superphosphates are especially adapted. — Many experiments in Europe, supported by results in this country, show that few if any plants respond more quickly or more favorably to superphosphates than the turnip. Coming in the same category close behind the turnip may be mentioned the cabbage and the other closely related plants such as Brussels sprouts, kale, kohl-rabi, and cauliflower, also many of the quickly maturing garden crops, such as lettuce, beets, spinach, and radish.

Superphosphates are especially adapted to all cases where spring top-dressing is practiced, as, for example, on grass land, for clovers, alfalfa, and winter grains.

Certain writers for the agricultural press recommend, on the contrary, for such purposes basic slag meal and fine bone meal; yet it not infrequently happens that the rainfall is light after the spring applications have been made; and instances have occurred where, for several weeks after the fertilizer was applied, hardly more than one-fourth of an inch of rain has fallen. Under such circumstances grass crops have been increased from two to two and one-half tons per acre by the top-dressings, in which acid phosphate was used, whereas if the phosphoric acid had been applied in bone or in basic slag meal, it would have been practically without effect on the grass

crop of that season. Indeed, the consequences which must follow in such cases, if phosphates insoluble in water are used, are too obvious to require further illustration.

The use of liberal amounts of superphosphates, especially in conjunction with generous applications of nitrogenous and potassic fertilizers, has been found to be especially helpful in connection with the culture of the sugar beet; for by their use the maturity is hastened and the sugar content consequently increased. Similarly, the use of extra superphosphate for potatoes not only often increases the total crop, but also the percentage of starch, due chiefly to the hastening of maturity. The use of superphosphate is also helpful in some cases because by hastening maturity the crops may more surely escape frost.

Recent studies have shown that superphosphates aid the germination of seeds to a remarkable degree, as compared with other fertilizer ingredients.

CHAPTER XVII

POTASSIC FERTILIZERS

In earlier times wood-ashes and the ashes of sea-weeds were the chief sources of potash, but at present the supplies for the entire world are practically all drawn from the German mines.

376. Wood-ashes and lime-kiln ashes. — Wood-ashes constitute one of the most ancient sources of potash, not only for industrial purposes, but also for use as a fertilizer. They may contain from 2.5 to 12 per cent or more of potash (potassium oxid, K_2O), dependent upon the temperature of the fire, the kind of wood used, and the freedom from impurities. As offered for sale in the United States, at present, the potash content usually ranges from 3 to 8 per cent. In addition, they contain from 30 to 35 per cent of calcium oxid, 3 to 4 per cent of magnesium oxid, and from 1 to 2.5 per cent of phosphoric acid, together with impurities and other ingredients of little or no fertilizing value.

Leached wood-ashes contain usually but from 0.3 to 1 per cent of potash, the quantity depending upon the thoroughness of the leaching.

Lime-kiln ashes, which consist of a mixture of waste lime and wood-ashes or coal-ashes, rarely contain more than from 1 to 2 per cent of potash.

377. Cotton-seed hull ashes. — A prominent source of potash, used very extensively at an earlier date for the growing of tobacco in the Connecticut Valley, was the

ashes produced in the burning of cotton hulls, known in the trade as "cotton-seed hull ashes." In the analysis of forty samples at the Massachusetts agricultural experiment station the potash content was found to range from 10 to 42 per cent, the average being 22.48 per cent; they also contain from 3 to 13 per cent of phosphoric acid, about 9 per cent of lime, and 10 per cent of magnesia. It is obvious that material ranging so widely in potash content should be bought only by analysis or on a definite guaranty.

378. Saltpeter waste. — A by-product known as saltpeter waste has been found by the Massachusetts experiment station to range in potash content from 5.6 to 13.7 per cent. The chlorin present amounted to 4.6 per cent, the sodium oxid to 37 per cent, and the nitrogen to from 0.52 to 3.3 per cent.

This material, like all factory by-products, can be bought with safety only on analysis.

379. Other wastes containing potash. — In addition to the foregoing, there are a vast number of other waste products, including prussiates, cyanid residues, and brick-kiln ashes, which are used for manurial purposes; but they usually contain widely variable percentages of potash, and some of them sometimes contain objectionable substances; for this reason they hardly deserve further mention in this connection.

380. Potash from sea-weeds and other plants. — Among the plants which serve as prominent sources of potash along the sea-coast, may be mentioned the marine algæ familiarly known as "sea-weeds." Incidentally unusual interest has just been aroused in the recovery of potash from sea-weeds, chiefly on account of difficulties with the German potash producers, due to contracts made between the owners of certain individual German mines

Compilation of Analyses of Certain Sea-weeds

(These analyses represent the composition of absolutely dry sea-weeds, *i.e.* those from which the water had been entirely expelled at a temperature of 100° C., the boiling point of water.)

Sea-weed	Month of Collection	100 Pounds of Dry Sea-weed contain					Analyst
		Nitrogen	Phosphoric Acid	Potash (Potassium Oxid)	Lime (Calcium Oxid)	Magnesia (Magnesium Oxid)	
		Lbs.	Lbs.	Lbs.	Lbs.	Lbs.	
Laminaria saccharina, ribbon-weed, kelp, tangle	January	1.85					H. J. W. & B. L. H.
	March	1.99	.46	2.83	2.76	1.55	H. J. W. & B. L. H.
	September	.94	.35	.80	3.28	1.39	H. J. W. & B. L. H.
		1.75	.58	1.10	1.49	.71	Eug. Marchand
	Aug. or Sept.		.93	5.02	8.24	3.03	O. Vibrans
Laminaria digitata, broad ribbon-weed, broad-leafed kelp, devil's-apron, tangle	January	2.26	.58	3.92	2.87	1.68	H. J. W. & B. L. H.
	March	2.27					H. J. W. & B. L. H.
	September	1.34	.23	.68	2.57	1.31	H. J. W. & B. L. H.
			.48	4.18	2.21	1.39	Gödechens
		1.07	.54	1.18	1.74	1.04	Eug. Marchand
Rhodymenia palmata,[1] dulse, dillisk . . .	January	3.50	.84	9.95	6.35	.97	H. J. W. & B. L. H.
	September	1.92	.53	5.84	.63	.33	H. J. W. & B. L. H.
Ascophyllum (*Fucus*) *nodosum*, round-stalked rock-weed	January	1.50	.38	2.93	2.03	1.54	H. J. W. & B. L. H.
	March	1.18	.38	2.77	2.10	1.50	H. J. W. & B. L. H.
	September	.64	.30	2.74	2.28	1.54	H. J. W. & B. L. H.

[1] Portions of this sea-weed were covered with minute shells, and the quantity was greatest in January.

			.22	1.46	1.86	1.59	Gödechens
			.32	3.77	1.79	1.24	Anderson
		1.75	.38	3.16	1.77	1.88	Jenkins
	March	3.06	.58	3.52	1.74	1.39	Conn. State Exp. Sta.
Fucus vesiculosus, flat-stalked rock-weed	January	2.03	.45	2.05	1.67	1.24	H. J. W. & B. L. H.
	March	1.93	.60	2.77	2.04	1.34	H. J. W. & B. L. H.
	September	.82	.40	3.14	1.84	1.22	H. J. W. & B. L. H.
			.19	2.12	1.36	.99	Gödechens
					2.07	1.87	James
			.84	2.64	1.15	1.67	Forchhammer
		1.09	.37	3.61	1.54	1.01	Anderson
			.45	1.32	7.74	2.50	O. Vibrans
		1.09	.35	1.40	2.42	1.71	C. E. Bergstrand
	March	3.06	.57	3.45	1.73	1.47	Conn. State Exp. Sta.
		1.22	.34	.95	2.22	1.01	Eug. Marchand
Phyllophora membranifolia[1]	January	3.49	.39	2.28	15.71	2.03	H. J. W. & B. L. H.
	March	2.78	.41	2.80	19.20	2.34	H. J. W. & B. L. H.
	September	3.36	.48	3.62	8.99	1.66	H. J. W. & B. L. H.
Chondrus crispus, Irish or Carrageen moss	January	2.84	.69	5.11	2.68	1.37	H. J. W. & B. L. H.
	March	3.10	.57	3.67	1.09	1.49	H. J. W. & B. L. H.
	September	1.32	.40	3.69	2.07	1.37	H. J. W. & B. L. H.
			.08	3.57	1.48	2.34	Forchhammer
	March	4.02	.89	5.22			Conn. State Exp. Sta.
Cladostephus verticillatus	January	1.57	.78	4.92	3.02	1.25	H. J. W. & B. L. H.
Zostera marina, eel-grass, grass-wrack	January	1.73	.16	.67	3.23	2.14	H. J. W. & B. L. H.
	March	2.78	.46	2.29	2.47	1.45	H. J. W. & B. L. H.
	September	1.13	.42	2.17	2.41	1.43	H. J. W. & B. L. H.
			1.18	3.37	11.81	.98	O. Vibrans
		1.28	.75	2.96	2.87	.17	Mass. State Exp. Sta.
		1.28	.29	.28	3.61	.16	Mass. State Exp. Sta.
			1.23	1.14	3.32	2.21	W. H. Bergen
Polyides rotundus	September	3.30	.60	1.44	2.40	.72	H. J. W. & B. L. H.
Ahnfeldtia plicata	September	1.69	.39	3.50	.88	1.11	H. J. W. & B. L. H.

[1] A large number of small shells adhered to the samples taken in January and March, and a less number to those secured in September.

and certain groups of American fertilizer manufacturers. It has, in consequence, been again proposed to make use of the enormous masses of sea-weeds available on the Pacific coast. This is no new idea, for sea-weeds have been thus utilized in the past, and even certain salworts (*Salsola*) have been expressly cultivated, collected, and burned in Spain, Sicily, and elsewhere, and the fused ashes sold under the trade name of " barilla." Ashes of these plants from near the Caspian Sea are said to contain 5 per cent of potash which is readily soluble in water.

In earlier times straw and weeds of various kinds were used for the manufacture of both sodium and potassium carbonates. At various times it has been proposed to utilize for this purpose wormwood, tansy, the common marigold, and other plants rich in alkalies.

381. Analyses of sea-weeds. — Many analyses of sea-weeds common on the New England coast have been made by Wheeler and Hartwell,[1] and these, with analyses by others, are given in the tables on pages 230 and 231.

382. Tobacco stems. — Tobacco stalks and the waste midribs from the leaves are often sold as " tobacco stems." The Massachusetts agricultural experiment station reports six analyses of such material showing the potash content to range from 3.76 to 8.82 per cent. With a moisture content of 10.6 per cent, the average potash percentage was found to be 6.44. Such tobacco stems are also rich in nitrogen besides containing small quantities of lime and magnesia. The potash present in the dried stems may be very largely removed by mere extraction with water, and even the insoluble potash residue must, in the process of decomposition, become very readily available to plants.

[1] Bul. 21, R. I. Agr. Exp. Sta., January, 1893.

383. Indian corn cobs. — It has been shown that Indian corn cobs contain an average of about 6.8 per cent of potash and that the ashes made from them contain about 50 per cent of potash,[1] hence the ashes of corn cobs have a greater total fertilizing value, per ton, than muriate of potash or the high-grade sulfate of potash.

384. Potassium nitrate. — One of the oldest and best known sources of potash, until the discovery of the German potash deposits, was "niter," or potassium nitrate. This material usually contains from 12 to 14.5 per cent of nitrogen, in addition to 44.5 to 45.5 per cent of potash.

Potassium nitrate is especially valuable for agricultural purposes wherever it is desirable to avoid the sulfuric acid and chlorin which are present in the German potash salts. Unfortunately, the supply is so limited, and the price in consequence so high, that it only occasionally comes into close competition with the German potash salts and the Chilian nitrate of soda. Nevertheless, there have been several years during the last two decades when the American farmer might have effected a decided saving in the purchase of his fertilizer supply had he bought potassium nitrate instead of the usual potash salts and nitrate of soda.

A discussion of the methods used in the manufacture of potassium nitrate are to be found elsewhere (Section 241).

385. Potassium carbonate. — In the Caucasus there exist many factories for the manufacture of potassium carbonate, which is sold on the basis of 90 per cent of pure potassium carbonate. The chief impurities are sodium carbonate, 5 per cent; potassium sulfate, 2 per cent; and potassium chlorid, 6.5 per cent. In 1906 eleven such factories were reported in Russia. This material, like

[1] E. S. R., *17* (1905–1906), 1054.

potassium nitrate, is also to be recommended whenever chlorids and sulfates must be avoided; but it is more applicable to soils of an acidic character than to those well supplied with basic ingredients. If used in large quantities, it has a tendency to dissolve humus and to bring about deflocculation of the mineral matter, and consequently its use on certain soils may be disadvantageous.

386. History of the German potash deposits. — The German potash salts, which to-day constitute one of the most valuable possessions of any country of the world, were at the outset looked upon as a hindrance in the production of common salt.

Salt works had already existed in Stassfurt, Germany, for a long period of time. They were at first the property of the Duke of Anhalt, they then passed into other hands, and in 1796 were sold to the Prussian "Fiscus." In the years from 1830 to 1840 common salt was discovered by borings made south of the Harz Mountains, in the Thuringian basin. The brines there were so favorable for the manufacture of salt that the weak brine at Stassfurt could not be used in successful competition with them, and hence the Stassfurt works were finally closed in 1860.

On April 3, 1839, a boring was begun at Stassfurt, and in 1843 at a depth of 256 meters the upper covering of the salts was met. It was then continued for 325 meters in the salt, without reaching the bottom of the deposit. The result of this undertaking was entirely unexpected, as well as a great disappointment at the outset, for instead of securing a saturated solution of common salt the saline solutions also contained large amounts of magnesium chlorid and potassium chlorid. It was concluded, however, by Doctor Karsten and Professor Marchand that

at greater depths common salt would be met, and in 1852 the sinking of two shafts was begun. At the end of five years common salt was found at a depth of 330 meters; but in reaching the deposit it was necessary to penetrate 250 to 280 meters of potassium and other salts.

Soon thereafter similar discoveries were made at Neu Stassfurt, Löderburg near Stassfurt, and at Douglashall near Westeregeln. In a word, boring followed boring, not only north of the Harz Mountains, but to the southward and elsewhere, and mine after mine was opened at such frequent intervals as to increase the number, soon, to more than 150, thereby taxing the ability of the newly organized German potash syndicate to control the situation.

387. Americans buy a German potash mine. — Finally the Virginia-Carolina Chemical Company of the United States purchased a German mine, and on July 1, 1910, when the proposed renewal of the German potash syndicate failed, large contracts for potash salts, continuing for several years, were made by certain mine owners with American fertilizer manufacturers.

388. The famous potash contracts. — The reign of high prices for potash salts and the end of the former great German monopoly seemed now to have arrived. At this juncture the Reichstag passed a measure, practically creating a government monopoly of the potash salts. This situation soon led to diplomatic exchanges on the subject between the United States and Germany. As a result of this and subsequent agitation a new syndicate was formed, and the American contracts have finally been otherwise adjusted or withdrawn.

389. Mode of occurrence and distribution of potash deposits in Europe. — In the course of the search for these saline deposits in Germany, it has been found that they are

not confined to any particular geological formation, for they occur from the Permian to the Tertiary, though the deposits near Stassfurt underlie the "Bunter" sandstone of the Triassic period.

The following shows the arrangement of the deposits in the order from top to bottom in which they are more commonly found in the vicinity of Stassfurt: —

Alluvial deposits.

Diluvial deposits.

"Bunter" (Brown) sandstone (Triassic).

Gypsum, anhydrit, red clay, etc.

Newer common salt (a later secondary formation, frequently lacking).

Anhydrit (anhydrous calcium sulfate).

Salzthon.[1]

Carnallit region.

Kieserit region. "Abraum" salts.[2]

Polyhalit region.

Older common salt.

Anhydrit.

Frequently kainit is found in the upper part of what is essentially the carnallit region, but its presence is not universal.

Schönit, sylvanit, and many other minerals also occur in these deposits, though not usually in great quantities.

390. The chemical composition of the more important potash salts is given in the following table: —

[1] The Salzthon is made up of three layers, consisting at the bottom of calcium sulfate, in the middle of magnesia (uncombined) and alumina, and at the top of clay and from 40 to 50 per cent of magnesium carbonate. This forms an impervious and protecting cover for the potassium and magnesium salts below.

[2] A term applied because these salts were over, and in the way of getting at, the common salt, which necessitated their removal.

AVERAGE PERCENTAGE COMPOSITION OF GERMAN POTASH SALTS OF AGRICULTURAL IMPORTANCE

NAME OF SALT	POTASSIUM SULFATE, K_2SO_4	POTASSIUM CHLORID, KCl	MAGNESIUM SULFATE, $MgSO_4$	MAGNESIUM CHLORID, $MgCl_2$	SODIUM CHLORID, NaCl	CALCIUM SULFATE, $CaSO_4$	MATERIAL INSOLUBLE IN WATER	WATER	ACTUAL POTASH, K_2O	
									Average	Guaranteed Minimum
Natural Crude Salts										
Kainit	21.3	2.0	14.5	12.4	34.6	1.7	0.8	12.7	12.8	12.4
Carnallit		15.5	12.1	21.5	22.4	1.9	0.5	26.1	9.8	9.0
Sylvanit	1.5	26.3	2.4	2.6	56.7	2.8	3.2	4.5	17.4	12.4
Kieserit ("Berg")		11.8	21.5	17.2	26.7	0.8	1.3	20.7	7.5	
Concentrated, Manufactured Salts										
I. Sulfates predominating, nearly free from chlorids:										
Sulfate of potash, 96 per cent	97.2	0.3	0.7	0.4	0.2	0.3	0.2	0.7	52.7	51.8
Sulfate of potash, 90 per cent	90.6	1.6	2.7	1.0	1.2	0.4	0.3	2.2	49.9	48.6
Sulfate of potash and magnesia	50.4		34.0		2.5	0.9	0.6	11.6	27.2	25.9
II. Chlorids predominating:										
Muriate of potash, 90–95 per cent		91.7	0.2	0.2	7.1		0.2	0.6	57.9	56.8
Muriate of potash, 80–85 per cent		83.5	0.4	0.3	14.5		0.2	1.1	52.7	50.5
Muriate of potash, 70–75 per cent	1.7	72.5	0.8	0.6	21.2	0.2	0.5	2.5	46.7	44.1
Potash manure salts, minimum 20 per cent of potash	2.0	31.6	10.6	5.3	40.2	2.1	4.0	4.2	21.0	20.0
Potash manure salts, minimum 30 per cent of potash	1.2	47.6	9.4	4.8	26.2	2.2	3.5	5.1	30.6	30.0

391. Duration of the deposition of potassium salts. — In the common salt are to be found thin bands of anhydrit which have been taken to represent the records of yearly deposits of gypsum during the colder season of the year. Based upon this and other features connected with the deposits, it was estimated, in 1864, that they might have been formed in 1500 years; but later estimates [1] place the time at from 10,000 to 13,000 years. At all events there seems to be no doubt that the deposition took place in a salt inland lake either fed by springs or having for a long time a continued or intermittent connection with the ocean.

392. Natural deposits of potassium salts elsewhere. — Up to the present time no discovery of large and important deposits has been made aside from those in Germany and a few in Austria. The occasional rumors of really important discoveries in the United States still lack confirmation. The discovery of such deposits at any time need not, however, be a matter of surprise, for it would seem that elsewhere than in Europe, lying above the salt deposits of like origin, the potassium and magnesium salts of the mother liquors may likewise have crystallized out; and they may also have been similarly preserved from the action of water by a natural protecting cover, just as they are by the "Salzthon" in Germany.

393. Kainit. — The most important of the natural salts, used directly as a fertilizer, is kainit (see analysis, p. 237), which, though it contains potassium sulfate, also carries large quantities of chlorids. It is used somewhat extensively in Europe, due in part to the low transportation charges. Kainit has been employed to some extent in the

[1] Die Salzindustrie von Stassfurt und Umgegend von Dr. Precht, Stassfurt, 1889, p. 5.

United States for direct application to the soil, though its chief use has been in compounding " complete " commercial fertilizers.

The employment of kainit in fertilizer mixtures is usually indicated by the fact that their chlorin content, in such cases, is usually a little more than twice as great as the per cent of potash.

Because of its chlorin content, kainit is to be avoided in the growing of sugar beets and tobacco, and also in the production of potatoes, if they are intended for starch manufacture. This is due to the depressing effect of chlorin upon the starch and sugar content of certain plants, provided that the application is made in the spring in which the crops are grown. In the case of tobacco the chlorin affects injuriously the color of the ash, and also the burning quality. Extended experiments in Europe have disclosed the fact that good crops may be secured, and that this ill effect may be avoided, by using extra heavy applications of kainit in the year preceding the one in which these sensitive crops are to be grown, and by omitting it entirely the following spring. It has been found, in such cases, that no serious losses result from leaching, and the subsequent efficiency of the potash is not materially endangered.

394. Sylvanit and carnallit. — Another crude but less abundant salt, often applied directly to the land, is sylvanit. This consists chiefly of chlorids and contains about 12 per cent of potash. It is sold in Europe at a lower price than kainit.

Carnallit. — In Germany even the crude carnallit, containing about 9 per cent of potash, is also applied directly as a fertilizer; but it can neither be transported long distances nor can it be stored with safety in moist places because of its hygroscopic character.

395. Muriate of potash. — The manufactured potash salt exported most extensively from Germany is the muriate of potash. The grade chiefly employed in agriculture is the one containing from 48 to 50 per cent of potash, equivalent to from 80 to 85 per cent of potassium chlorid. The remaining 15 to 20 per cent consists chiefly of common salt, associated with small amounts of sodium and magnesium salts and a little water.

396. High-grade sulfate of potash. — The grade of sulfate of potash most commonly manufactured and sold for agricultural purposes in the United States is that containing from 47 to 48.5 per cent of potash, or about 90 per cent of potassium sulfate. This is usually designated as " high grade " sulfate of potash, in order to distinguish it from a lower grade which contains large amounts of magnesia, in addition to potash. The small amounts of other ingredients in this potash salt are given in the preceding table (p. 237).

397. Double sulfate of potash and magnesia, or double manure salt. — Following the foregoing manufactured potash salts in agricultural importance, in the United States, is the double sulfate of potash and magnesia, also known as " double manure " salt, containing from 25 to 27 per cent of potash, or approximately 50 per cent of potassium sulfate. The fact that this salt also contains 34 per cent of magnesium sulfate ($MgSO_4$), and that it is essentially free from chlorids, makes it especially applicable for soils which may possibly lack magnesia, and for situations where sulfur is possibly needed or where chlorin should be avoided.

This salt should not be employed as a source of potash on soils already relatively too rich in magnesia.

At the present time potash in the two sulfates costs,

in the United States, about one and one-quarter cents per pound more than in muriate of potash.

The double sulfate of potash and magnesia has been used by Goessmann and Brooks at the Massachusetts experiment station with especially good results, in combination with other fertilizing ingredients, in the manuring of apple trees.

398. Double carbonate of potash and magnesia.— The double carbonate of potash and magnesia is a hydrous salt, also prepared in Germany, which has been used in several instances with excellent results in the United States. The material, according to an analysis made at the Massachusetts experiment station, was found to contain 18.5 per cent of potash and 19.5 per cent of magnesia.

In experiments at the Rhode Island experiment station it was found especially helpful in cases where not only potash but also an alkaline treatment of the soil was demanded; hence it is to be recommended wherever magnesia is not already present in too great amounts and where muriate of potash and sulfate of ammonia either fail to produce their full effect or are toxic, because of an acidic condition of the soil.

399. Silicate of potash. — A silicate of potash for agricultural use, containing from about 24 to 27.6 per cent of potash, has been prepared in Germany and distributed in this country for experimental purposes. It was thoroughly tested by Brooks in Massachusetts and found to be a valuable fertilizer, ranking in efficiency between the muriate and the high-grade sulfate of potash. It is, however, of less interest than otherwise, because its manufacture is said to have been discontinued.

400. Potassium carbonate (Pearl ash). — Potassium carbonate (Pearl ash) and so-called "potashes," consisting

of potassium carbonate and potassium hydrate, have been used as fertilizers to a small extent, and also in compost heaps. The former compound has found considerable application in the growing of tobacco. In experiments at the Rhode Island experiment station, covering a period of seventeen years, it has been found to give, with most crops, materially better results on a silt loam soil of acid character than an equivalent amount of potash in muriate of potash. Had the soil been alkaline at the outset, or nearly so, doubtless the reverse might have been true, as was found by W. P. Brooks in certain experiments in Massachusetts.

401. Greensand. — A natural potash mineral of very low grade, but yet of some fertilizing value, which has been used more or less extensively as a manure, at points near where it occurs, is "greensand" or "greensand marl."

This has generally been supposed to be a sea-bottom deposit, but it has recently been asserted that similar zeolitic compounds are probably formed by the action of magmatic waters. Greensand occurs widely, but the deposits of chief interest in the United States are found in New Jersey. According to Cook, the material has an average content of about 5 per cent of potash, and it often contains in addition from 1 to 2 per cent of phosphoric acid. The greensand is a hydrated silicate of iron and potassium, a species of glauconite. Its action is slow, as might be expected, and the effects of a single heavy application are visible for a dozen years. It, like the other zeolites, is capable of being decomposed by hydrochloric acid, and hence it readily parts with the lime, magnesia, soda, and potash which it contains.

Much virtue is ascribed by many writers to these zeolitic

compounds by reason of the fact that the bases are mutually interchangeable, and because of the prominent part they are supposed to play in giving to the soil its ability to absorb and hold lime, potash, and magnesia, when they are applied for manurial or amendatory purposes.

It has been proposed by H. Wurtz [1] to utilize the greensand as a source of potash by fusing it with calcium chlorid, a method employed recently by Cushman and others for treating potash feldspars.

402. Phonolite, nepheline, alunite, leucite, and feldspars as sources of potash. — It was suggested long ago by Storer [2] and others that certain feldspars (orthoclase feldspar, $K_2O \cdot Al_2O_3 \cdot 6\,SiO_2$, if pure, contains 17 per cent of potash) might possibly be so finely pulverized as to make them valuable fertilizers. Especial interest was recently awakened in the subject by Cushman,[3] who claimed to have found feldspar, thus prepared, of decided value in the growing of tobacco.

It has been shown by F. Schacke, Tacke, and Popp,[4] and by H. von Feilitzen,[5] that powdered phonolite and nepheline ($(Na \cdot K)_2O(Al_2O_3 \cdot 2\,SiO_2)$) were of some value as potash fertilizers, but were far inferior to the German potash salts. The results with feldspar and with alunite were, however, too poor to make them worthy of consideration as practical potassic fertilizers. The value of finely ground feldspar has also been carefully studied by Hartwell and Pember.[6] They employed a finely ground product capable of passing a screen having

[1] Storer, Agriculture, *2* (1897), 487.
[2] Agriculture, *2*, 1897.
[3] Bul. 28, Office of Public Roads, U. S. Dept. of Agr.
[4] Chem. Ztg., *35*, 1222; Abs. Chem. Abstracts, *6*, 1048.
[5] Deut. Landw. Presse, *38* (1911), 737, 738.
[6] Bul. 129, Agr. Exp. Sta., R. I. State College.

No potassium | 11 grams ground potash feldspar (K_2O, 9.09 %) | 2 grams sulfate of potash

FIG. 24. — TREATMENT OF MILLET.

2.75 g. | 6.88 g. | 11.00 g. — Ground feldspar

0.50 g. | 1.25 g. | 2.00 g. — Sulfate of potash

No potassium

FIG. 25. — TREATMENT OF WHEAT.

200 meshes to the linear inch, and containing about 9 per cent of potash, 3 per cent of soda, and less than 0.4 per cent of lime. The work was done in pots which were supplied regularly with water to the optimum limit, whereby the conditions for bringing the potash into solution were far better than those usually met with in farm practice.

In the course of these experiments, beans, wheat, and Japanese millet (*Panicum crus-galli*) were grown. As a result it was found that the feldspar possessed such slight value as a fertilizer that no one could think of using it to replace the German potash salts.

It has been proposed that leucite ($K_2O \cdot Al_2O_3 \cdot 4\,SiO_2$), containing 22 per cent of potash, might be heated with salts of lime or soda whereby the solubility and efficiency of the potash for plant production would be increased. Although it is admitted that much is gained by such treatment, yet the product has never been placed in successful competition with the German potash salts.

CHAPTER XVIII

THE THEORY AND PRACTICE OF POTASH FERTILIZATION

The fact that the ocean contains far more sodium salts than potassium salts is explained on the ground that sodium is far more easily removed than potassium, from its zeolitic and other combinations, by the natural processes of leaching. This is also well illustrated by the well-known fact that in the natural weathering of certain basic rocks the relative potassium content increases progressively, whereas the relative sodium percentages become less.

403. The alleged ill effects of the chlorin of potassium and other salts. — According to A. Mayer,[1] calcium and magnesium chlorids are not particularly injurious to meadow grasses. It is asserted by L. von Wagner that chlorids are not good for beets and potatoes, but he doubtless refers to their depression of the sugar and starch content, which can be avoided by making the applications the preceding year.

It has been explained by O. Loew[2] that the ill effect of chlorids is probably due to the liberation of hydrochloric acid in the plant cells and to the fact that, unlike nitric and sulfuric acids, little of it is assimilated, on which account the accumulation soon reaches toxic limits.

In discussing the beneficial action of the carbonate, sul-

[1] Lehrbuch der Agrikulturchemie (1886), 295.

[2] Bul. 18, U. S. Dept. of Agr., Div. of Veg. Phys. and Path., p. 18.

fate, nitrate, silicate, and phosphate of calcium, Ullmann[1] says that calcium chlorid is injurious to plant life.

It is stated by Griffiths,[2] based upon observations by Jamieson and Munro, that potassium chlorid is a plant poison and that investigations in England and on the continent of Europe have shown it to be an unreliable potash manure. It must, however, be recognized that the danger was greatly overdrawn by Griffiths in view of the fact that enormous quantities of muriate of potash are used throughout the world, with unquestionably good results.

Certain early experiments by Nobbe,[3] with buckwheat, have been very generally cited in the past in support of the alleged benefit derived by plants from chlorin, but A. Mayer[4] holds that Nobbe attached undue weight to the matter. Nevertheless, observations on potatoes by Pfeiffer[5] are said to indicate that chlorin was helpful, yet Pagnoul found, on the contrary, that chlorin was injurious to the growth of potatoes when grown on a sandy (silicious) soil. It should be recalled in this connection that ammonium chlorid has also been used by some experimenters with good results, whereas others consider it a plant poison.

404. Reasons for the diversity of ideas concerning chlorids. — In an attempt to throw light on the reason for the quite contrary views of so many leading authorities, Wheeler and Hartwell[6] experimented with several different chlorids. Calcium chlorid was highly toxic to potatoes on an acid soil, but either caustic magnesia or slaked lime was shown to be capable of correcting the condition.

[1] Kalk und Mergel (1893), 9.
[2] A Treatise on Manures, p. 225.
[3] Landw. Vers.-Sta., *6*, 118; also *13*, 398.
[4] Landw. Vers.-Sta., *49*, (1901).
[5] Landw. Vers.-Sta., *49*, 349–385.
[6] 15th An. Rpt. R. I. Agr. Expt. Sta. (1902), 289–304.

Magnesium chlorid was not found to be toxic for barley under the same conditions, yet ammonium chlorid was exceedingly toxic. In the latter case the toxicity was wholly corrected by calcium carbonate. The same result was also secured with caustic magnesia, after allowing ample time for it to become well carbonated in the soil. In other experiments in which ill effects were observed from the use of muriate of potash, these were completely overcome, and the fertilizer was made to produce normal results by the employment with it of basic slag meal or other basic substances.

In field experiments at the Rhode Island experiment station, potatoes of excellent cooking quality have been grown annually, with few exceptions, for a period of twenty years with muriate of potash as the sole source of potash. These results followed, even though the potash salt was applied in the spring, immediately before planting. Slaked lime had, however, also been applied periodically to the soil, which may have been an important factor in bringing about such a result.

From these various experiments it appears probable that the highly toxic effects, reported as due to chlorids, may often have been caused, in consequence of a lack of basic substances in the soil. In fact, Schultz, of Lupitz, demonstrated conclusively that occasional applications of marl were necessary on the light acid soil of his section of northern Germany, in order to insure good results from repeated applications of the German potash salts.

It has been pointed out by H. Ley [1] that neutral salts prevent or check dissociation. It is possible, therefore, that the lessening or hindering of unfavorable dissociations,

[1] Ber. der deut. chem. Gesell., *30*, 2192.

induced in the soil by the use of chlorids, may account in some measure for the benefit derived from lime and other basic substances.

405. The use of chlorids increases the need of liming. — When chlorids of potassium and other bases are used on soils well supplied with carbonate of lime, double decompositions result whereby the chlorin unites with the lime and magnesia, forming the corresponding chlorids. These chlorids, in reasonable quantities, are not only not observably toxic in the presence of an excess of carbonate of lime; but, owing to their high solubility, they readily leach away in seasons of heavy and frequent rainfall. This is true especially if the chlorid of potassium is applied a few months, or preferably the autumn or spring, preceding the growing of such crops as are most subject to injury by chlorin.

Muriate of potash is reported by many as giving usually slightly greater yields of potatoes than the sulfate of potash, though the tubers are often claimed to be of inferior cooking quality. In regions of heavy rainfall, and where plenty of lime is used, the danger in this respect seems to be greatly lessened or overcome.

406. The fate of sulfate of potash in the soil. — Sulfates are less objectionable in the soil than the chlorids, for the reason that plants require and utilize considerable sulfur. Furthermore under temporary or long-continued anaërobic conditions due to heavy rainfalls, sulfates are readily reduced by bacterial action, with the result that sulfids are formed from which even so weak an acid as carbonic acid may disengage hydrogen disulfid, at the same time forming carbonates.

When sulfate of potash is employed on soils rich in lime, one result of the exchange of bases is the production of

calcium sulfate. This salt is relatively insoluble, for about 400 parts of water are required to effect the solution of 1 part of it, whereas calcium chlorid soon liquefies upon exposure to the air.

On this account, especially if the conditions are occasionally favorable to reduction, the soil may not become so rapidly depleted of its supply of lime when using sulfate of potash as when muriate of potash is used.

407. Concerning the retention of potash by soils. — It was already known in the time of Aristotle that common salt is partly removed from solution upon leaching it through sand or soil. It was also shown by Way, in 1850, that when sulfate and muriate of potash are applied to ordinary soils, the sulfuric acid and chlorin appear in the drainage waters combined with lime and magnesia, and that the potash is held quite completely and tenaciously in the soil in zeolitic (zeolites are combinations of alumina, silica, water, and the bases lime, magnesia, soda, or potash, or various combinations of these bases) and other mineral and organic chemical combinations.

It is now maintained by physicists and physical chemists that the phenomenon of absorption may embrace three distinct processes: (1) a mechanical inclusion called imbibition, illustrated by the absorption of water by a sponge or by soil; (2) the partial taking up of the dissolved substance to form a new compound or a solid solution [1] such as is claimed to result in the absorption of phosphoric acid, by lime, or by ferric oxid; (3) absorption which is

[1] A solid solution is a crystalline, amorphous, homogeneous solid capable of changing its composition with the changing concentrations of the liquid solution in contact with it. A definite compound, on the other hand, is "stable in contact with a liquid solution of its constituents over a measurable range of concentration."

the concentration or condensation of the substance in solution on the surface of the absorbing medium.

It has been held by Cameron that potash is probably held in soils by absorption.

Notwithstanding that in laboratory experiments, in which relatively small amounts of soil are usually employed, the removal of potassium from weak solutions of potassium sulfate and of muriate of potash is never complete; yet the conditions are entirely unlike those in field operations, in which the amount of material is most minute in its relation to the great volume of soil. It may, nevertheless, be true that on sandy soils, which are greatly deficient in clay, silt, and vegetable matter, potash salts may, in extreme cases, be subject to moderate losses by leaching, and they should consequently be used with some caution.

408. The teachings of the Rothamsted investigations. — In the drainage waters from the unmanured experimental plots of the Broadbalk wheat field at Rothamsted, Voelcker found 1.7 parts of potash per million, whereas in the drainage waters from the other plats receiving as much as 300 pounds of sulfate of potash per annum, he found only 2.9, 3.3, and 4.5 parts per million. An examination of the same soils by Dyer showed that about half of the potash applied, in excess of that removed by the crops, during a fifty-year period, was still present in the upper nine inches of soil, and much of it was still soluble in a 1 per cent solution of citric acid. Still further portions of the excess of potash were found in the second and third nine inches, which were also found to be soluble in the citric acid solution.

409. Various factors affecting absorption. — Absorption appears to be dependent upon at least the following factors: —

(1) The solubility of the given substance in the solvent employed, although the relation is as yet unknown.

(2) The character of the absorbing substance, though it

Full ration of sodium carbonate

Full ration of potassium carbonate

FIG. 26. — TREATMENT OF SPINACH.

Both lots limed and fertilized alike with nitrogen and phosphoric acid.

is uncertain in how far this is determined by the area of exposed surface and by the character of the surface involved.

(3) In a given solvent the rate of absorption of different substances in solution is variable, even with one and the same absorbing medium. This is so marked in some cases that partial separations of two different salts in the same solution may be thus made.

(4) Selective absorption from electrolytes, as when potassium chlorid is filtered through soil, cotton, or other absorbents. In this case the filtrate not only becomes less concentrated, but even contains free hydrochloric acid.

(5) The rate of absorption increases with the concentration of the solution and with the amount of the absorbent or of its effective surface.

410. Potassium essential to plant growth. — It is fully accepted that potassium is absolutely essential to plant growth, even notwithstanding that it may, for many kinds of plants, be partially replaced by sodium, in connection with one or more of its possible functions. The degree, however, of even this partial replacement appears to be largely dependent upon the particular kind of plant involved.

411. Potassium aids carbohydrate formation. — It has been found that the curtailment of the potassium supply exerts a serious effect upon the formation of carbohydrates, such as starch, sugar, and cellulose; and in actual field practice certain crops especially rich in starch and sugar seem to require its liberal employment.

412. Other functions of potassium. — It is now also held that potassium performs valuable functions in the formation of the proteins, and that it aids cell and nuclear division. It has also been asserted by Loew that potassium acts as a condensing agent, which would facilitate the building up of carbohydrates from formaldehyde, as Loew has previously suggested.

413. Potassium increases the size of the individual grains of cereals. — In experiments by Hellriegel and Wilfarth it was found that, with the supply of phosphoric acid or of nitrogen curtailed, the quantity of grain was greatly lessened; but yet the weights of the individual kernels were but slightly, or not at all, affected. When, however, the supply of potash was curtailed, the size of the individual grains became smaller, and the formation and translocation of starch was soon interfered with or prevented.

In the later years of the barley experiments at the Rothamsted experiment station, after a lack of potash became evident, it was found that the average weight of the grain per bushel for a period of fourteen years was greater where potassium salts were used in the fertilizer, and the average weight per kernel was increased thereby in an even far greater degree.

414. Effect of potassium on photosynthesis. — Other experiments at Rothamsted with mangel wurzels show that with the leaf production varying but little, the addition of potassium salts to the other fertilizers increased the yield of roots nearly two and one-half times. When these roots were analyzed, it was found that the increase in weight was due almost wholly to the increased production of sugar and of other carbohydrates. It would appear, therefore, that the process of photosynthesis in the leaf and the consequent possibility of the storage in the roots of the products elaborated by the leaves, is largely regulated by the potash supply available to the plant. In this instance the crop of roots was increased, as a result of the use of the potassium salts, from 12 to 29 tons and the total product of sugar from 0.797 ton to 2.223 tons.

415. Potassium in connection with turgor. — Notwithstanding that many writers even yet refer to "the function" of potassium salts as if potassium performed only the function which has just been discussed, it appears probable that there may be several. It has even been asserted by Copeland [1] that potassium is both a direct and indirect factor in maintaining the turgor of the plant. The importance of this conclusion may, however, be doubted in view of the work of De Vries,[2] who, though upholding for a time the importance of certain organic acids in maintaining turgor, concluded later that growth may occur without turgor and that rapid growth may lessen it. It is also asserted by Pfeffer that turgor cannot furnish the energy essential to growth, but that on the contrary it is a result of the conditions of growth.

416. The functions of potassium not necessarily shown by the result which its absence produces. — As concerns the association of potassium solely with the function of aiding in the formation and translocation of starch, Pfeffer [3] is of the opinion that phosphorus may be as necessary in that respect as potassium, and he affirms "that the function of an essential element is by no means directly indicated by the result which its absence produces."

417. Potassium as a neutralizer and carrier within the plant. — It has been pointed out by Shimper [4] that organic acids are the normal product within the plant of the synthesis of the proteins. In experiments by Mercadente [5]

[1] Bot. Gazette, *24* (1897), 411.

[2] Bot. Ztg. (1879), 848.

[3] The Physiology of Plants, translated by Ewart (1900), I, 141.

[4] Zur Frage der Assimilation der Mineralsalze durch die grüne Pflanze.

[5] Abs. Jahresb. Agr. Chemie (1885), 257.

in which he grew certain species of *Oxalis* and of *Rumex* without potassium, it was found that only one-eighth of the normal amount of acid was produced, and that the oxalic and tartaric acids formed were in combination with lime. In this case, only small amounts of starch and sugar were present in the sap of the plants. It is known that the neutral and more especially the acid salts of potassium and oxalic acid which are normally formed in these plants, are toxic to them if they accumulate in undue quantities. Nevertheless, it has been suggested by Wheeler and Hartwell that potassium perhaps performs a valuable office in the plant by forming soluble combinations with some of these acid synthetical by-products, in which state they may be readily transported to other parts of the plant, where by their combination with lime they are transformed into comparatively insoluble and non-toxic compounds, and are eliminated from the circulation. In this case potassium would not only act as a neutralizer, but also as a convenient and even necessary transporting medium.

418. Potassium may contribute to the "luxury consumption" of plants. — It has been shown by careful investigation in Germany that a certain minimum of lime, magnesia, potash, and soda is essential to plant growth, but that plants require, nevertheless, a certain excess of bases above these total minima which may be supplied indiscriminately by any one or more of them; for this reason, if there is a lack of the other bases, potassium may be helpful by virtue merely of supplying this so-called (though necessary) "luxury" consumption.

419. Certain functions and effects of potassium salts in soils. — In some cases potassium salts may perform a useful function in the soil by virtue of increasing the surface tension of the soil solution, by which the rate of the

capillary movement of water toward the surface and toward the plant roots is increased.[1] It is also asserted by King (*l.c.*) that the presence of salts in the soil lessens evaporation from the surface, so long as they remain in solution, and if they crystallize out they serve in a measure as a mulch.

Attention has recently been called by Müntz and Gaudechon [2] to benefit which they allege may result in certain cases from the addition to soil of soluble fertilizer salts, since they lower the vapor pressure of the water and induce a distillation, to the affected points, of water vapor from the soil below and from the air above.

If soils are too open, the use of the German potash salts may gradually improve their physical condition, by virtue of the fact that they react with calcium carbonate, if present, to form potassium carbonate, which salt has a highly deflocculating action. If, on the contrary, a soil is exceedingly fine, like many clay soils, the potassium carbonate may by the same action injure the existing conditions, rendering the soils too compact and consequently difficult to till. It may make them at the same time also less suited in other respects to support plant growth to the best advantage. In these particulars the varying effects are analogous to those resulting from the residual soda of nitrate of soda (Section 254).

420. The effect of potassium salts on legumes. — The beneficial effect of potassium salts upon clover and other legumes has long been generally recognized, and many soils which have been found to be deficient in potash have come to be termed "clover sick." It is nevertheless true that clover sickness may sometimes be due to a lack

[1] King, Text-book of the Physics of Agriculture (1901), p. 106.

[2] Compt. rend., *48* (1909), 253–258.

of lime, to disease, or other conditions; and one is not necessarily justified in assuming which of the various causes of the failure of clover may need to be dealt with, without special knowledge of the particular locality and of the soil concerned.

In view of the known promotion of the fixation of atmospheric nitrogen by certain plants, including the legumes, when the associated bacteria are well supplied with carbohydrates, it appears that at least one way in which potassium salts may be helpful to the legumes is by increasing the carbohydrate supply within the plant, by which the organisms of the root nodules are made to work more effectively.

In the permanent grass experiment at the Rothamsted experiment station, the herbage in 1902, where a mineral fertilizer containing phosphates, sulfate of potash, magnesium salts, and sodium salts had been used in the past, was 55.3 per cent legumes; whereas where potassium salts were omitted from the fertilizer mixture, the legumes amounted to but 22.1 per cent; and where nitrogen was applied and the potassium salts were omitted, no legumes were to be found.

421. The effect of a lack of potassium on grasses and other plants. — On the plots of land at Rothamsted where potash was most deficient, the grasses very largely failed to produce seed and the stalks were weak and brittle. This was assumed to be due to an insufficient development of carbohydrates within the plants. It is further mentioned by Hall that the grass possessed an abnormal color, lacked chlorophyl, and exhibited other signs of malnutrition. The leaves of Swedish turnips developed under similar conditions a " flecked " appearance, mangel wurzels were attacked by a leaf-spot fungus (*Uromyces*

betæ), wheat developed much rust, even when little was present elsewhere, and grass was attacked by various fungi.

Whether the ill effects arising from a deficiency of potash were due to a lack of general vigor or to an altered composition of the plant cells, Hall does not attempt to conclude, although he inclines to the former view. Concerning these results, Hall cautions against giving too much weight to such effects, in general farm practice, since the manurial conditions were most unusual and had been developed during the long term of years in which the experiments had been in progress.

422. Potassium salts act best in wet seasons. — The effect of potassium salts upon wheat and barley, at Rothamsted, has been found to be far more favorable in wet than in dry seasons, due possibly to its preventing premature ripening. The yield of barley in a dry season was 18.1 bushels per acre without the use of potassium salts, whereas it was 30.8 bushels when they were employed. In a wet season the yield in the first instance was 34.9 bushels, and in the latter instance 41.4 bushels, per acre. It has been found, in the case of root crops, that potash hastens maturity; however, in barley and wheat the migration processes are quite different from those involved in the storage which takes place in root crops.

423. A lack of potassium more serious for some crops than for others. — In the course of experiments which have been in progress at the experiment station of the Rhode Island State College since 1894, it has been found, where potassium salts were omitted from the otherwise complete fertilizer and sodium salts substituted for them, that clover and timothy (*Phleum pratense* L.) largely, and in some cases completely, disappeared. Nev-

ertheless, moderate crops of redtop (*Agrostis vulgaris* With.) were still produced, although the plants gave evidence of probable faulty seed development. Where the potassium salts were omitted, dark spots appeared on the leaves of potatoes, and even a blackening of the entire leaf surface often resulted. This did not appear like, nor was it recognizable microscopically as being identical with, either the early or late blight of potatoes. The plants, as would be inferred, died prematurely.

Notwithstanding that the conditions in this experiment and in those at Rothamsted were quite unusual, it may nevertheless be true that under conditions which exist in farm practice instances sometimes occur where plant diseases may become unusually severe, due to a lack of potash or of a sufficient supply of other plant food ingredients, to insure normal plant development.

424. Potash conservation in the soil by sodium salts. — It has been shown by Wilfarth and his co-workers at Bernburg, Germany; also at Rothamsted; and by Wheeler and Hartwell in Rhode Island, that certain plants, when supplied liberally with sodium salts, take up materially greater quantities of it, and less of potash, than when no sodium salts are applied. In fact, in the case of the Rhode Island experiments, the conclusion seemed obvious that plants supplied with the necessary minimum of potash could, perhaps with equal advantage, use some soda to replace a part or all of the excess of potash which they might have removed from the soil, had it been present. It appears, therefore, that nitrate of soda and the sodium compounds associated with the German potash salts may conserve, somewhat, the potash stores of the soil by preventing a "luxury," or unnecessary, consumption of potash by the plant.

CHAPTER XIX

LIME AND ITS RELATION TO SOILS AND FERTILIZERS

LIME has been shown not only to be a corrective, in the presence of an excess of magnesia or of certain other substances, but also to be absolutely essential to plant growth, and incapable of complete replacement by other plant food ingredients.

425. The occurrence of lime. — Lime is present in combination with carbonic dioxid and also with alumina and silica in many of the representative rocks of the earth's crust. It may be present in soils in the form of minute crystals of apatite, or in other combinations of lime with phosphoric acid; likewise in gypsum (calcium sulfate), calcium carbonate, in zeolitic compounds, and as a constituent part of decaying vegetable matter.

426. Distribution and effect of limestone. — Carbonate of lime is widely distributed in the form of rock, and in many respects it is the most important form of lime found in soils.

Notwithstanding the wide distribution of limestone rocks over most of the globe, there are nevertheless soils upon which it appears probable that lime is sometimes even needed as plant food, though perhaps in such cases only in connection with restricted classes of plants. Generally, however, if lime is required at all, it is as a soil amendment, either in a neutralizing or flocculating capacity. As a neutralizer it exerts a powerful influence upon

the character of the microscopic soil flora, thus vitally affecting ammonification, nitrification, denitrification, and nitrogen assimilation.

Lime also affects the development of certain diseases, not only on the roots, but also on the aërial portions of plants.

It is because of these many functions of lime in the soil and of the many cases of contradictory effects, dependent upon the character of the soil, upon the kind of plant grown, and upon the particular plant disease involved,

Fig. 27.

Clover, where before liming it could not be grown successfully. It was said to winter-kill, which was really seldom the case.

that the problems connected with the use of lime are of a very complex character.

427. Kinds of lime used in agriculture. — "Burned" lime, "rock" lime, "stone" lime, and "builder's" lime are various names given to the final product after the carbon dioxid of limestone or marble has been expelled by heat. In this process 100 pounds of pure limestone (calcium carbonate) lose about 44 pounds of carbon dioxid and yield about 56 pounds of calcium oxid (CaO, or lime). Most limestone is so impure that the product, after burning, usually contains not more than from 95 to 98 per cent

of lime; and certain highly magnesian limestones yield, upon burning, a product containing about 60 per cent of lime and about 40 per cent of magnesia.

Dolomite is the most highly magnesian of limestones, and it contains before burning 30.4 per cent of lime and 21.7 per cent of magnesia.

Magnesian limestones are common, yielding a burned

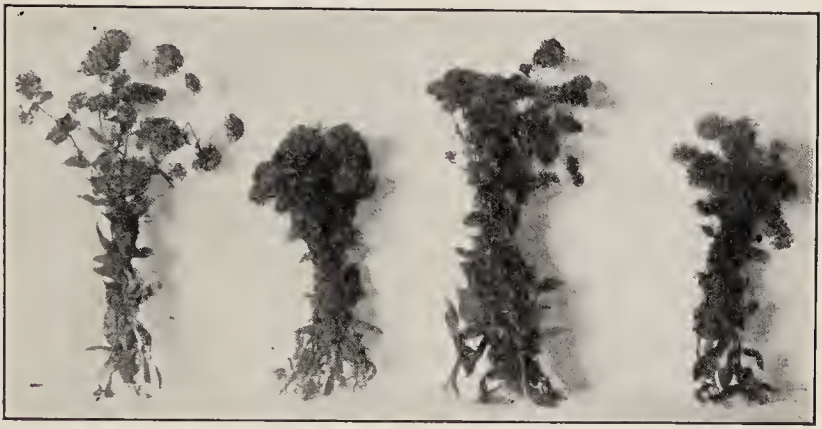


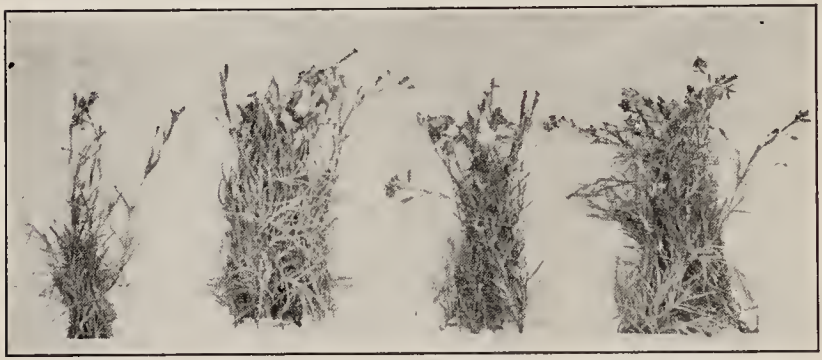
FIG. 28. — TREATMENT OF *Silene orientalis*.
All fertilized alike with potash and phosphoric acid. A like amount of nitrogen was used in each case.

product containing amounts of magnesia ranging from the merest traces to about 40 per cent.

Burned limestone is often ground, without slaking, and sold, without further treatment, for direct application to the land. In other cases the lime is slacked by the addition of about one-third its weight of water, when there results a fine, dry product known as " water-slaked," or more commonly as " hydrated " lime ($Ca(OH)_2$). This is proportionately poorer in lime than before slaking, on

account of the addition of the hydroxyl groups (OH). Frequently lime is slaked by mere exposure to the air, whereby it takes on water and carbon dioxid, forming a mixture of calcium carbonate and calcium hydrate. Upon long and complete exposure to the air, under the most favorable conditions, hydrated lime and air-slaked lime become practically reconverted into calcium carbonate.

Other sources of carbonate of lime for agriculture pur-



Unlimed Limed Unlimed Limed
Sulfate of ammonia Nitrate of soda

FIG. 29. — CARNATIONS.

All fertilized alike with potash and phosphoric acid. A like amount of nitrogen was used in each case.

poses are wood-ashes, the waste from the manufacture of acetone, soda, and from other industrial processes.

The chief materials used for furnishing carbonate of lime are, however, ground shell marl, ground oyster shells, and ground limestone or marble. These are named in their order of availability. Ground limestone and marble are the least efficient, chiefly on account of their crystalline structure.

428. The effect of lime on nitrogen availability. — It

often happens in soils which are deficient in carbonate of lime that the application of burned, air-slaked, or hydrated lime, ground limestone, or marl has an almost immediate beneficial influence upon ammonification and nitrification.

Cases are on record where the efficiency of certain forms of organic nitrogen, in soils, has been increased from two to a dozen times, solely as the result of a single heavy application of lime.

429. The effect of lime on denitrification. — The effect of lime on compact clay or silt soils is to cause several small particles to draw together by the process known as "flocculation." As a result, the air more readily enters the soil, whereby the conditions are usually rendered less favorable for the destruction of nitrates, since denitrification is essentially a reducing or anaërobic process. In fact, Koch and Pettit [1] have shown that in soils with 25 per cent or less of water the denitrifying organisms lie quiescent, but when the moisture content is increased, destruction of nitrates begins suddenly; and considerable nitrogen is then liberated in the gaseous state It appears probable that the critical percentage of moisture would be found to vary somewhat with the physical character of the soil.

430. The effect of lime on soil texture. — As suggested in the preceding paragraph, liming greatly improves compact silt and clay soils, especially if they are in such condition that they tend to bake badly. This improvement is not only due to hindering denitrification, but also in consequence of the general effect of a more free circulation of air, the creation of conditions more favorable to nitrification, and finally, also, by virtue of increasing the penetra-

[1] Centralb. f. Bakt., II Abt., *26* (1910), 335–345, Abs. E. S. R., *23* (1911), 123.

bility of the soil by water, whereby surface erosion is greatly lessened. The storage of water in the soil is also increased, and its subsequent capillary movement is better regulated and adapted to properly supplying the needs of the plants. Such soils, after being suitably limed, are fit to work much earlier in the spring than those from which lime has been omitted.

It is also true of light sandy and gravelly soils that the use of lime often improves their condition by the mere adding of fine material, which increases their lifting capacity for water. Furthermore, it is claimed that by the chemical combination of the lime with silica and alumina to form zeolitic compounds, the condition of the soil is not only rendered better from a physical standpoint, but also as concerns its ability to hold potash and other plant food elements.

The physical character of light soils is also said to be affected favorably by the adherence of lime to the surface of the existing soil particles.

In all cases heavy liming is to be avoided on light soils, especially in hot climates, and particularly if they are greatly deficient in vegetable matter. In no case should opportunity be lost to increase the supply of the latter, even though lime is used with great care and in small quantities.

431. The use of lime in connection with phosphates. — The presence of calcium carbonate in soils may be expected to insure that when superphosphates of any kind are applied to them, some of the monocalcium phosphate will revert with lime rather than entirely or chiefly with oxids of iron and aluminum, as might otherwise be the case. This is quite commonly of distinct advantage in view of the fact that the phosphates of iron and aluminum, when

once formed, are considered as being less available sources of phosphoric acid for plants, at least on acid soils, than tricalcium phosphate. They are also less soluble than the latter in weak acids, including even carbonic acid.

Large applications of burned or slaked lime, or even of carbonate of lime, are said to be frequently important factors in liberating phosphoric acid already locked up in the soil in combination with iron and aluminum oxids, as has been pointed out by Dehérain.[1]

The beneficial effect of applications of slaked lime upon the subsequent efficiency of roasted iron and aluminum phosphate, even for several years after the last application of each, has been most strikingly demonstrated at the agricultural experiment station of the Rhode Island State College.[2] This benefit is usually assumed to be due to the long-continued reactions resulting from the gradual transformation of the calcium carbonate into the more active bicarbonate, which then reacts more effectively than the carbonate upon the iron and aluminum phosphates. It is possible likewise that other more complex factors are also involved.

432. Lime as a destroyer of worms and slugs. — Much has been written of the effect of lime in destroying worms and slugs, and Storer [3] states that if but 3 to 4 tons of lime are applied per acre, some insects may escape destruction, but that it may be expected to be very effectual if from 7 to 8 tons of lime are applied per acre. It must be recognized, however, that on sandy or other light soils one should seldom, if ever, use more than from 1000 to 2500 pounds of burned or slaked lime per acre, in a single ap-

[1] Traité de Chemie Agricole (1892), 525.
[2] Buls. Nos. 114 and 118.
[3] Agriculture, *2* (1897), 545.

plication. It is but rarely that more than from 1 to 2.5 tons per acre would be required, on heavier soils, in order to accomplish such changes as are immediately desirable. For this reason it is believed that the practical significance of liming, as a remedy for slugs and worms under usual economic agricultural conditions, has been unduly emphasized.

It has been suggested by English writers that freshly slaked lime or, preferably, burned lime should be scattered in clover fields or in stubble where insect pests are common. This should be done, however, at or after dusk, or before sunrise, since the effectiveness of the lime depends upon its coming into direct contact with the worms or slugs, which appear to be unable to withstand its caustic action.

433. Need of liming suggested by soil acidity. — Soils are commonly referred to as acid which quickly and intensely redden a blue litmus paper when brought in contact with it under suitable conditions of moisture. Unless such soils are very light and sandy, or are typical subsoils, they usually yield immediately, without previous extraction with hydrochloric acid, dark chocolate, brown, or black extracts, upon stirring them with water and dilute ammonium hydroxid.

It has been pointed out by Cameron and others of the Bureau of Soils of the United States Department of Agriculture, that finely divided or porous substances which can in no way be considered as acid, as, for example, cotton, have, nevertheless, the property of absorbing the base away from blue litmus paper, whereupon it gradually takes on the color of the acid or red litmus. It should be remarked, however, that this reaction between litmus paper and cotton takes place very slowly. On account of these and similar observations and because some soils

which impart a red color to litmus paper have not shown subsequent benefit from liming (conclusions drawn sometimes without sufficient attention to the requirement of the particular plant), the reliability and value of the litmus paper test for ascertaining if soils are in need of liming, has been seriously questioned from several sides. It has been shown,[1] however, that, notwithstanding this physical absorptive property of soils, such reddening of blue litmus paper does not result in the presence of moisture and of calcium bicarbonate. Again, if a considerable amount of

[1] Bul. 139, Agr. Expt. Sta., R.I. State College.

FIG. 30. — MANGELS WITH VARIED TREATMENT.

All fertilized alike with potash and phosphoric acid. A like amount of nitrogen was used in each case. Note the better effect of the nitrate of soda than of the sulfate of ammonia on both limed and unlimed soil. Beets of all kinds are greatly aided by the sodium when potassium is deficient, and nitrate of soda also lessens soil acidity.

active calcium carbonate is present in a soil, the rain water, and the soil solution charged with more or less carbonic acid derived from the air, and from decomposing plant residues in the soil, must inevitably react with it to form calcium bicarbonate, the quantity of which would increase within certain limits with the quantity of carbonic acid present. For this reason the rapid and intense reddening of blue litmus paper by a moistened soil, whatever the reaction may be ascribed to, is an indication of a sufficient lack of basic substances to possibly interfere with suitable bacterial development and with the growth of certain higher varieties of plants, unless lime or other basic substances are employed.

434. Liming the most economic basic treatment. — Whether, therefore, a soil is strictly acid or is sufficiently lacking in bases to require their addition, even if for other reasons than for the neutralizing of acidity, liming is suggested as a suitable remedy. In fact, no other basic treatment, excepting possibly in some cases with magnesia, is either so economical, so lasting, or is it followed by such general good results, as liming.

435. Chemical methods for determining the lime requirements of soils. — Many methods have been proposed from time to time for determining the lime requirements of soils, as, for example, (1) the adding of lime-water to the soil, evaporating, and determining the lime remaining uncombined, and (2) the bringing of soil in contact with calcium carbonate and the measurement of the carbon dioxid evolved either at the usual or higher temperatures. In the latter case the period of treatment must be very brief, on account of the progressive destruction of organic matter and the consequent liberation of carbon dioxid from it, which is in no way related to the reaction sought.

Soils are sometimes extracted with water, and the watery extract is titrated by use of a suitable indicator, taking cognizance of the probable presence of free carbonic acid in the extract.

The foregoing are but a few of the methods proposed for the quantitative measurement of the lime requirement of soils, but all fall short of perfection for practical purposes for the reason that they may give the total of basic absorption and chemical combination, or they may give only a fraction of this requirement. The true end point of the reaction in some cases is difficult to determine, and, furthermore, the amount of lime actually demanded to give the best results can only be approximated for certain selected groups of plants, and even the individual members of a group may vary among themselves in this respect. It is also true that amounts of lime far less than are shown by some of these quantitative tests are actually preferable, for certain crops, to the full amounts indicated.

It is nevertheless true that certain of these methods, in the hands of one having a practical knowledge of the differences in plant requirements, when applied to unknown soils in conjunction with tests of soils the requirements of which have been previously determined, may have very great value. On the other hand, however, they may lead to very erroneous and faulty conclusions as to the treatment, if placed in the hands of one having solely a knowledge of the chemical and laboratory side of the problem.

436. The effect of lime on vegetable decay. — It is mentioned by Storer that lime performs valuable functions in the soil by coagulating organic matter.

If burned or slaked lime is mixed with relatively fresh

vegetable matter, the first effect is to retard decomposition, but if decay has already progressed to a considerable extent, its introduction, in reasonable amounts, is likely to hasten decomposition almost from the outset. In fact, the action of lime in compost heaps is generally so well understood as to require no more than passing mention.

Lime is also highly important in hastening ammonification and the subsequent formation of nitrates from vegetable matter; because, in order that nitrification may be active and progressive, there must be present some base

FIG. 31. — CRANBERRIES UNDER VARIED TREATMENT.

All fertilized alike with potash and phosphoric acid. A like amount of nitrogen was used in each case. The cranberry is shown to thrive best on soil so acid as to be destructive to mangels.

such as lime, magnesia, potash, or soda to combine with the nitric acid as it is formed, for otherwise the accumulation of acid soon inhibits the activity of the nitrifying organisms.

437. The effect of lime on nitrogen content of humus. — It must be remembered that in the early stages of the destruction of vegetable matter, the losses of carbon and hydrogen are relatively great, due to their ready transformation under usual soil conditions into water and carbonic acid. Thus the organic residue becomes for a time, on

the percentage basis, continually richer in nitrogen. In this connection it should be stated that it has been shown, on a soil greatly in need of liming which was kept for many years chiefly in hoed crops, that liming lessened to a considerable extent the total humus removable by extraction with ammonium hydroxid ("matière noire" of Grandeau), but that the percentage of nitrogen in the humus was distinctly greater than before, thus showing the same general action of lime on material already well humified, in an acid soil, as on vegetable matter in a less advanced stage of humification. This tendency of the nitrogen percentage to rise, after liming, is of interest in connection with observations by Hilgard and others to the effect that the higher the percentage of nitrogen in the humus, the greater becomes the availability of its nitrogen to plants. This helps also to explain the high fertility of soils well supplied with calcium carbonate which have become heavily charged with decaying plant residues.

438. Rational rotation and the turning under of sward should accompany liming. — The ideal condition is reached when a grass, clover, alfalfa, or other sod, plenty of barn-yard manure, straw, or green crops are introduced into the soil with sufficient frequency to maintain a suitable supply of vegetable matter with which to insure proper tilth. This material also furnishes food to the organisms which assimilate atmospheric nitrogen and at the same time, through the action of lime, yields carbonic acid to act upon the mineral constituents of the soil. These residues also furnish to the plant considerable supplies of available nitrogen as ammonia and soluble organic matter, but primarily as nitrates.

439. Avoidance of liming to conserve humus not wise. — The idea that organic matter should be kept from de-

struction in the soil as long as possible, and that liming should be avoided because it hastens such destruction, is wholly exploded by the recent investigations of the microscopic soil organisms and of their several beneficent functions; nevertheless, liming should not be overdone.

Sufficient lime in its burned, hydrated, or air-slaked condition, or as calcium carbonate, should be applied, to

FIG. 32. — ASPARAGUS DIFFERENTLY TREATED.

All fertilized alike with potash and phosphoric acid. A like amount of nitrogen was used in each case. It should be noted that a fourth bundle is lacking at the left. This was because every plant died on the plot which received sulfate of ammonia but no lime.

bring about a reasonably rapid humification of the vegetable matter, but at the same time care must be taken that this latter supply is reasonably maintained. In this connection it should be stated that it is universally understood that the repeated employment of slaked or burned lime in unduly large quantities without stable manure, green manures, the turning under of sward, and without proper fertilization must be avoided, or dire consequences are

likely to follow. This is not only true as concerns the exhaustion of available potash and phosphoric acid, but also because of the serious destruction of the vegetable matter already in its various stages of decomposition. Nevertheless, the frequent sweeping condemnation of the use of slaked or burned lime without regard to the cost of transportation and other conditions affecting its use is equally to be avoided. On account of their ready availability, such forms of lime should usually be applied at intervals of from four to seven years, and, if employed on suitable soils, in reasonable quantities, and at the right point in such rotations as involve the periodic turning under of a good grass sod, no fear of material injury to the land need be entertained.

440. Carbonate of lime *versus* slaked or burned lime. — At the present time in the United States certain experiments conducted at the agricultural experiment station of the Pennsylvania State College are being extensively cited in the agricultural press, and elsewhere, as a basis for the unqualified denunciation of the use of burned and slaked lime.

Conditions of the Pennsylvania experiment. — In the foregoing experiment, however, neither fertilizer nor stable manure was used. Slaked lime was applied at the rate of two tons per acre every four years, immediately before Indian corn in a rotation of Indian corn, oats, wheat, and clover. In comparison with it, like amounts of calcium oxid were used in ground limestone. In the former case the liming should preferably have preceded the seeding to wheat and clover, and the order of the rotation should have been reversed to give an opportunity for a favorable trial of the slaked lime. In the case of the limestone the application was divided into two equal parts, each

being applied in alternate years, thus giving it a distinct advantage. As a result of the excessive quantity used, and of the application of the slaked lime at the wrong point in the rotation, it actually depressed many of the yields of Indian corn.

The quantity of lime applied in the Pennsylvania experiment in twenty years on the basis of the four applications, assuming a content of 70 per cent of calcium oxid, was 11.200 pounds of actual calcium oxid per acre. The soil was furthermore not greatly in need of liming, as has

No lime Ground limestone Hydrated lime

FIG. 33. — ALFALFA WITH TREATMENT UNDER FARM CONDITIONS.
All fertilized alike with potash and phosphoric acid. Quantities of lime having the same total neutralizing value were used in each case.

since been shown by Brown, and as indicated also by the fact that no great injury arose from several repeated applications of ammonium sulfate on other plots. It appears, therefore, that slaked lime was not only applied at an unfavorable time, but also in excessive quantities.

Slaked lime highly beneficial in the Rhode Island experiments. — In striking contrast to the foregoing results, slaked lime has been used most successfully during a period of twenty years in several crop rotations at the agricultural experiment station of the Rhode Island State College, on land so greatly in need of lime at the out-

set that beets, spinach, and lettuce could not be grown successfully without it or other alkaline fertilizers or manures. This soil was, furthermore, so greatly in need of lime that a single small application of sulfate of ammonia became immediately toxic. It is interesting to note, however, that even under these extreme conditions the total quantity of calcium oxid employed (including any magnesium oxid present) was equivalent to less than 3200 pounds of calcium oxid, per acre, in an interval of nineteen years. Even though in most of the instances in the Rhode Island experiments, fertilizers were applied exclusively, the crop yields, as a rule, have been well maintained, and in general less fertilizer has been used in the later than in the earlier years.

The preceding experience shows, therefore, that too much alarm should not be occasioned by the results of experiments which have been conducted under unnatural conditions, and with unreasonably large quantities of slaked or burned lime.

Slaked lime becomes quickly carbonated. — It must further be borne in mind that recent investigations have shown that slaked and burned lime, if applied in reasonable amounts, change quickly in the soil into the form of calcium carbonate; hence it is essentially, as concerns subsequent effect, as if it had been applied as such at the outset. In the course of earlier experiments made by Heiden, he concluded that in some cases lime remained in a caustic state in the soil for years; it appears, however, that he assumed that all lime found soluble in water and capable of producing an alkaline reaction was necessarily present in the soil as calcium hydrate. The falsity of this assumption is evident in view of the fact that calcium carbonate, if placed even in distilled water, is somewhat soluble and will

FIG. 34. — CANTALOUPES DIFFERENTLY TREATED.
All fertilized alike with potash and phosphoric acid. A like amount of nitrogen was used in each case.

cause it to give an alkaline reaction. Furthermore, carbonic acid, which is always present in the rainfall and in the soil water, increases decidedly the alkaline reaction, by virtue of forming calcium bicarbonate. Again, salts of lime formed by other weak acids may themselves give an alkaline reaction in water. This experiment by Heiden has been widely cited by various writers as a reason why hydrated or burned lime should not be applied to soils, yet had they taken the pains to investigate the circumstances, it would have been found that the conclusion of Heiden was not justified by the experimental method which was followed.

The bearing of the Maryland station experiments. — Still another experiment, made at the Maryland agricultural experiment station, has been generally cited in the United States as showing great superiority of calcium

carbonate over slaked or burned lime. In this case the soil was admittedly deficient in both available potash and phosphoric acid, and it was only in certain of the eleven years covered by the experiment that any fertilizer was applied, although its need was indicated by the small size of the crops which were harvested. In this case marl and ground oyster shells were compared with stone lime and burned oyster shells, as well as with burned magnesia. It appears, however, upon an investigation of the circumstances that the total quantity of marl probably contained from 400 to 450 pounds of potash and approximately 48 pounds of phosphoric acid, and that these substances may readily have become limiting factors in connection with the yields. In fact, it seems probable, in the light of this circumstance, that enough available potash and phosphoric acid may have been secured by the crops from the marl, in many or all of the cases, to have accounted for the greater yields which it often produced. As concerns ground oyster shells, they often contain nearly .5 per cent of nitrogen and over .1 per cent of phosphoric acid, which may have given them some advantage over the burned lime.

The fine matter associated with the marl used in the Maryland experiments may have improved the physical character of the soil. It is especially significant, likewise, that in some cases the burned magnesia and burned oyster shells actually gave larger crops than at least the ground oyster shells. It appears probable, also, that the Maryland plots were not, in all cases, sufficiently uniform in character to justify some of the conclusions which have been drawn by others from the experiment. In view of this fact, and of the other circumstances mentioned, undue weight has apparently been attached to these results as a basis

for discrimination against slaked or burned lime. In fact, Director Patterson, who made the experiment, still recommends slaked lime for many agricultural purposes.

Views of certain eminent European authorities. — In conclusion it should be said that such eminent European authorities as Dehérain in France, and Orth in Germany, though fully familiar with the dangers which may arise from the unintelligent and inordinate use of burned or slaked lime, nevertheless, recognize the great agricultural value of these forms of lime in specific cases, when used in

No lime | Lime as top-dressing in spring after seeding | Lime harrowed in before seeding

FIG. 35. — TIMOTHY. ALL SEEDED THE SAME AUTUMN.
The lime in both cases was from the same lot, and was weighed out at the same time.

reasonable amounts, and under ordinary conditions of culture.

441. The penetration of lime into soils. — One of the usual recommendations regarding lime is to harrow it into the surface of the soil, for the reason that it tends to work downward. There can be no doubt but that the various forms of lime will be carried downward to a considerable extent both by mechanical washing and in solution as bicarbonate and otherwise, especially in soils which are sandy and open, and which are relatively deficient in vegetable matter.

On upland soils which are very compact, like certain silts and clays or fine soils containing large quantities of vegetable matter in advanced stages of decomposition, the chance for the descent of lime to the lower levels, excepting as it leaches through as nitrate, is very small, unless excessive amounts are used. This has been well illustrated by the experience of Coville, who attempted to introduce lime-water into the lower levels of a soil rich in vegetable matter, only to find that all of the lime was held in a comparatively thin layer of the surface soil.

Another striking example of lime being retained in the surface soil is afforded in connection with the renovation of some of the acid peat (hoch-moor) soils of northern Germany. After liming, and other suitable treatment, these soils bore good crops for a few years, only to be followed later by frequent serious failures. Subsequent investigation showed that this failure was due to the fact that the upper layer of soil had become so thin, as a result of the decompositions induced by the lime and by the system of drainage, that the crops suffered from drought by virtue of the fact that their roots did not penetrate to a sufficient depth to avail themselves of the permanent water supply. In fact, the lime had been of little or no value as a soil amendment below the level to which it was originally introduced, and the unlimed acid peat beneath was such an inhospitable medium that the plant roots would not penetrate it to any practical extent. The unfortunate condition was corrected by subsoiling with a plow carrying knife attachments in the rear, and lime in a hopper on the beam, by which means lime was incorporated with the lower levels of the soil, after which the conditions for plant growth were again found to be favorable.

The fact that plant roots will not readily penetrate an

inhospitable medium has been recently demonstrated by Reed in connection with some ingeniously devised experiments conducted in the laboratory of the Bureau of Soils of the United States Department of Agriculture.

442. The expulsion of ammonia from soils as a result of liming. — Experiments by Boussingault and others are often cited to show that so long as lime remains in the soil, in a caustic state, the formation of ammonia progresses. Observations are also on record showing that

FIG. 36. — ALFALFA UNDER TREATMENT.
All fertilized alike with potash and phosphoric acid. A like amount of nitrogen used in each case.

actual losses of ammonia from limed soils have been noted in laboratory experiments; and likewise in fields, after heavy liming. In most pot experiments, however, the proportion of lime to soil will be found to have been far greater than those existing in practical field operations; and even the applications of lime in the field were usually excessive and beyond what would be employed in rational agricultural practice. At all events, on all ordinary clay, silt, or loam soils the absorptive and chemical combining power of the soil for ammonia is so great that no material losses need be feared, wherever only reasonable applica-

tions of slaked or burned lime are made. This has been fully established at the experiment station of the Rhode Island State College, by both pot and field experiments, in connection with which applications of from 1 to 4 tons, per acre, of slaked lime have been made.

It has been observed, on unlimed soil, where sulfate of ammonia has been used, that ammonium salts, consisting chiefly of the carbonate or bicarbonate, sometimes appear on the surface as an efflorescence, some time after the sulfate of ammonia is applied; and in case the former salt were formed, losses of ammonia would be expected to occur. Where lime was employed, and the conditions for nitrification were better, no such efflorescence has ever been noticed. It therefore appears probable that there are cases where the retention by the soil of the nitrogen applied as ammonia, may be actually furthered by the employment of lime.

What has preceded illustrates the danger of generalizing from laboratory experiments, in which quite unusual conditions often prevail, or from field experiments in which excessive applications of lime have been used, as to what will transpire under the usual and normal conditions of farm practice. Nevertheless, such data serve as a constant and useful warning to those who must deal with very open, sandy soils, to the effect that there may be danger of serious direct loss of ammonia if either slaked or burned lime is used on them in excessive amounts.

443. The influence of lime on nitrification. — The influence of lime in promoting nitrification is now too well understood to require more than mere mention. It, or some other base, is essential to combine with the nitric acid as produced, and hence to prevent the uncombined nitric acid from accumulating to such an extent as to

inhibit the further action of the nitrifying organisms. For this purpose slaked lime, burned lime, or carbonate of lime may be used; although if either slaked or burned lime is employed, care should be taken not to use excessive quantities, for large amounts of slaked or caustic lime may check nitrification for a time. Such an apparent delay of the process of nitrification, for about ten days, resulted in one instance from the use of four tons of slaked lime, per acre, at the agricultural experiment station of the Rhode Island State College, on a good silt loam soil.

FIG. 37. — CHICORY UNDER DIFFERENT TREATMENTS.
All fertilized alike with potash and phosphoric acid. A like amount of nitrogen was used in each case.

It was noted, however, that no such delay followed the use of one ton of slaked lime per acre. At the end of the ten days the plants, in the first case, practically all recovered their normal appearance and made vigorous growth within forty-eight hours after the first sure signs of improvement were noticed. This improvement was doubtless coincident with the time when, by natural carbonation in the soil, the alkalinity of the lime had been reduced below the point where it could check the development of the nitrifying organisms. This experience suggests the experiments by earlier English investigators who

found that nitrification would not progress in undiluted urine until the alkalinity was lessened by the addition of calcium sulfate. This reacted with the ammonium carbonate to form the essentially neutral salts, ammonium sulfate and calcium carbonate.

It was found by Kellerman and Robinson that the addition of calcium carbonate to a sandy loam soil was favorable to nitrification up to a limit of 2 per cent, or to a far greater limit than would ever be applied to agricultural soils. The application of magnesium carbonate, however, in excess of 0.25 per cent positively inhibited the action of the nitrifying organisms.

444. Effect of calcium and magnesium carbonates on ammonification. — Experiments by Lipman[1] have shown that, when mixed with soil, calcium carbonate depressed the formation of ammonia from cotton-seed meal, but stimulated it in the case of dried blood; whereas with magnesium carbonate the result was exactly the opposite. This may have been due to the difference in the relative calcium and magnesium content of the blood and of the cotton-seed meal, whereby the relation of the two was made favorable in one instance, and unfavorable in the other, to the vegetative growth of the ammonifying organisms; as noted by Loew not only for certain lower organisms, but also for the higher agricultural plants. It has been suggested by Lipman that this difference in the action of the two carbonates upon organic matter of different kinds may explain the reason why the effect of magnesian lime is good on some soils and poor on others; also why where the magnesian lime fails, the purer lime is often helpful. Such practical differences in the action of the two carbonates as arise in farm practice may, however, not

[1] Centralb. f. Bakt., II Abt., *30* (1911), 173, 174.

only be due to the indirect effects suggested by Lipman and others, whereby more or less nitrogen is rendered available to the plants, but it may also be due to a direct physiological effect upon the agricultural plants themselves, which, according to Loew and his various co-workers, is often a very important factor in plant growth.

Recent investigations by Gile in Porto Rico appear to show that much wider lime-magnesia ratios may exist, without causing injury to certain plants, than the conclusions of Loew and his fellow-workers would indicate.

445. General ideas as to the indirect manurial action of lime. — Lime has long been looked upon, whether applied as hydrated, air-slaked, or fully carbonated lime, as a liberator of potash in the soil. This has been supposed to be due chiefly to mass action, whereby it may replace other bases in the zeolites and other similar compound silicates. Lime has also been shown by Morse and Curry[1] to increase the amount of potash freed, even from feldspathic and other potash-bearing minerals.

446. Results with sodium and magnesium salts illustrate how lime acts indirectly. — An excellent illustration of a very similar liberating effect of magnesium and sodium is furnished by the experiments at the Rothamsted station in England in connection with the wheat crop. These results are given by Hall from 1852 to 1901 inclusive. Sodium sulfate, potassium sulfate, and magnesium sulfate were added singly to separate plots of land; to one plot all three were added, and a fifth plot was included from which all were omitted. In the course of the first ten years potassium sulfate gave smaller yields than any of the other sulfates, but where all were omitted the yields were markedly inferior. As time progressed the

[1] Bul. 142 (December, 1909), N. H. Agr. Expt. Sta.

yields secured with sodium sulfate and with magnesium sulfate became relatively less, and the result with potassium sulfate in the subsequent decades of the experiment approached somewhat closely those secured with the combination of all three sulfates. Bearing in mind the recent work of Hart and Peterson,[1] it might be thought that these sulfates had been helpful by virtue of supplying additional sulfur to the plants, rather than as a result of their having liberated potash. If, however, such need of sulfur had existed, it would have been expected that where it was applied the percentage in the ash of the crop would have been increased, which was not the case. It must, however, be recognized that this is not always the case with nitrogen and perhaps not with other of the necessary elements. In all cases, nevertheless, the potash percentage in the ash of the crop was materially increased. The per cent in the ash in the case where no sulfates were added was 9.91; the respective percentages found upon the addition of sodium sulfate and of magnesium sulfate were 14.68 and 14.87; whereas, as a result of the use of potassium sulfate alone the potash in the ash rose to 23.28 per cent. With all three sulfates it amounted to 25.89 per cent. These changes were not accompanied by increases in the percentages of either soda or magnesia.

447. Fixation of potash after liberation by lime. — Notwithstanding that, in agreement with others, lime was found by Morse and Curry to have a marked solvent action upon the potash of feldspars, yet in the presence of considerable clay the potash was not found to have been rendered soluble in water. This was probably due to its having been fixed by the zeolitic compounds of the clay as fast as it was freed from the feldspar. This possibility is

[1] Research Bul. 14 (April, 1911), Wis. Agr. Expt. Sta.

illustrated by experiments performed by Gerlach in which he found tricalcium phosphate more or less soluble in certain weak acids, yet in the presence of iron and aluminum hydroxids no phosphoric acid was found in solution even after long-continued action. It was ascertained, however, in this case, that the phosphoric acid had been transferred to the iron and aluminum oxids, which fixed it as fast as the acid released it from its combination with lime. It appears probable, therefore, that as a result of the interaction of the lime and feldspar, in the presence of the

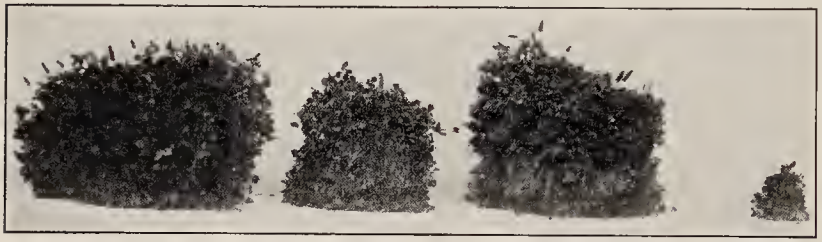


FIG. 38. — CRIMSON CLOVER UNDER TREATMENT.
All fertilized alike with potash and phosphoric acid. A like amount of nitrogen was used in each case.

clay, the potash of the feldspar may have passed to some extent into zeolitic combinations, as a result of which its subsequent availability to plants may have become greater than in its original combination. It is possible also that in the presence of the clay considerable lime was also absorbed or fixed by zeolites directly, whereby the action of the lime on the feldspar was greatly weakened. Indeed, Storer states that after submitting clay to the action of lime-water for a week or two, it will be found that an appreciable quantity of the clay which was previously insoluble in hydrochloric acid will then be dissolved, with

separation of gelatinous silica. In other words, by the addition of the lime to the clay, the formation of zeolites or compounds of similar character is apparently promoted.

448. Caustic lime attacks powdered quartz. — It has been shown by Stoeckhardt that caustic lime attacks not only precipitated silica, but also even powdered quartz previously extracted with acid, forming as a result hydrated calcium silicate.

The addition of carbonate of lime to soils often increases their power to hold potash, ammonia, and other bases, either by chemical or physical means, or perhaps by both. Furthermore, these bases may be set free again by the action of the sesquicarbonate or bicarbonate of lime which are continually being formed in soils stocked with active (the term "active" is used to designate such calcium carbonate as is not surrounded by particles of clay or other matter to such a degree as to be readily protected from attack by carbonic acid) carbonate of lime.

449. Losses of lime by leaching. — There are continual losses of lime from the soil due to various causes: —

(1) Carbonate of lime is even somewhat soluble in pure water, and certain salts in the soil solution are likely to increase the solvent action, as, for example, sodium chlorid, sodium sulfate, and certain ammonium salts.

(2) The presence of carbonic acid carried to the soil in the rainfall, formed by absorption of carbon dioxid from the air, and produced by the decomposition of vegetable and animal matter in the soil, insures the gradual formation of calcium sesquicarbonate and of calcium bicarbonate which may pass in some cases to a certain extent into the drainage water. The solubility of calcium carbonate has been shown to increase, at least within certain limits, with the amount of carbonic acid in the solution.

(3) In the nitrification of manures, fertilizers, and of plant or animal rêsidues in the soil, considerable calcium nitrate is formed which, not being held readily by the soil, is likely to be lost in the drainage unless the nitric acid therein is taken up by growing crops. At most seasons of the year and under favorable soil and cultural conditions, excepting in the case of a long-continued and excessive rainfall, there is but little loss by this means.

(4) A considerable depletion of lime results in soils from the use of sulfate of potash, or sulfate of magnesia, but more especially from application of potassium, sodium, and magnesium chlorids, since the resulting calcium chlorid is far more soluble than calcium sulfate. Furthermore, in case the soil is well stocked with vegetable matter and it becomes so wet as to temporarily exclude the air, calcium sulfate may be reduced to calcium sulfid, which in contact with carbonic acid may be decomposed into hydrogen disulfid and calcium carbonate, whereby some carbonate of lime is regenerated in the soil.

(5) Other salts of lime are also somewhat soluble and may in consequence add to the losses by drainage.

It is on account of these and other tendencies to loss of lime by natural drainage, and on account of the transformation of the calcium carbonate into other chemical combinations in the soil, that care must be taken to insure in soils at all times a small supply of " active " carbonate of lime.

450. Coarsely ground limestone compared with fine limestone and marl. — It is on account of the continual loss of lime from the soil by drainage that most of the soils of the humid regions which are formed from conglomerates, granite, gneiss, certain shales, schists, and sandstones, are usually deficient in lime. For the same reason

soils of limestone regions lying even but a few feet above marl, chalk, or limestone beds often become sufficiently exhausted of their carbonate of lime to require its supply to the surface soil.

It must be obvious from what has been said that the coarser the particles of lime added to the soil, the longer some of them will remain as calcium carbonate, or, in other words, the longer some effect of a given application

No lime Ground magnesian limestone Ground limestone

FIG. 39. — ALFALFA TREATMENT ON FARM.

All fertilized alike with potash and phosphoric acid. Quantities of lime having the same total neutralizing value were used in each case. On certain other soils in the same State, ground magnesian limestone was found to be superior to the ordinary ground limestone.

will endure. It is, however, false philosophy to assume that the lime which endures longest in the soil is necessarily either the most efficient or the most economical. It is, nevertheless, possible that there is a limit of fineness which permits of the preparation of ground limestone in a single grinding operation, a high percentage of which will pass a sieve with from 30 to 60 meshes to the linear inch, at such low cost that it is better economy to use more of the coarser material than a smaller quantity ground to a greater degree of fineness. If, in each case,

the same amount of material, passing a 30 or 50 mesh screen, can be secured at the same price, the still coarser associated material will cost nothing, and hence the purchaser might do better, if the transportation charges were low, to buy the coarser product.

In other cases it may be better to use less of a fine, readily available, and efficient product, and to repeat the application at more frequent intervals, than to buy, for a larger sum of money, coarser material which, even though some of it will remain in the soil longer, will nevertheless tie up a large cash investment for a longer period of time. No definite rule can therefore be applied to these cases, since the fineness and character of the product, the rate of interest, the character of the soil, the freight charges, the cost of hauling by team, and other factors must determine the choice of the purchaser in individual cases.

451. Concerning the practical use of lime. —Burned lime, finely ground or crushed, may be used at rates ranging from a quarter of a ton on certain light soils to two and one-half tons on extremely acid soils which are rich in humus, capable of immediate extraction with ammonium hydroxid. A third more, in weight, of air-slaked or hydrated lime may be used under the same circumstances, or somewhat more than double the quantity of ground limestone or marl.

Care should be taken to learn from small experimental plots about what quantities of lime are necessary, on a given soil, to insure success with the special crops to be grown; and this amount will often be found to be far short of the total "lime requirement," as indicated by certain quantitative laboratory methods.

Excessive liming is something to be especially avoided, for the natural tendency of farmers is to carry it to ex-

tremes as soon as the advantages from the use of lime have once been fully recognized.

On rocky pastures which cannot be plowed, lime must obviously be applied to the surface; and for this purpose ground limestone, or, preferably, shell marl or wood-ashes, are much to be preferred to burned or slaked lime.

On mossy lands, in bad general condition, small applications of some form of lime may be made to advantage just before plowing; but the chief part of the application should be made afterward, when it should be immediately

Limed Unlimed Limed Unlimed
Nitrate of soda Sulfate of ammonia

FIG. 40. — WATERMELONS VARIOUSLY TREATED.
All fertilized alike with potash and phosphoric acid. A like amount of nitrogen was used in each case.

and thoroughly harrowed into the soil. In all such cases the principle should be borne in mind that the nearer a particle of lime can be brought to each particle of soil, the better will be the result.

For most purposes, in ordinary farm practice the harrowing of the lime into the soil after plowing is to be recommended, though on land which cannot be plowed, carbonate of lime may be spread broadcast on the sod in order to bring in clover and certain nutritious grasses which may otherwise fail to thrive.

452. Pure lime compared with magnesian lime. — Instances are on record, as in the experiments by Pat-

terson,[1] in which burned magnesia in certain instances has given better results than burned lime, and there are, for example, certain soils, as in parts of New Jersey and elsewhere, upon which magnesian lime gives generally better results than pure lime. The reverse is also true in still other localities in New Jersey and elsewhere in other states. This is usually due to the presence in the soil of relatively much greater quantities of magnesia than of lime, and in such cases the use of highly magnesian lime may sometimes become objectionable.

Within a few years new and important light has been shed on the whole question by Loew and his various coworkers, which will be discussed in full in considering magnesia.

As a general rule it is at least erring on the safe side if one avoids liming repeatedly with a highly magnesian lime, and uses, alternately, a purer grade of lime.

[1] Bul. 110, Md. Agr. Expt. Sta. (1906), 13–21.

CHAPTER XX

LIMING IN ITS RELATION TO PLANTS

The subject of liming is just as important in its relation to plants as in its relation to soils and fertilizers, and in this respect the complexity of the whole question becomes increasingly great with each new research which is conducted.

453. Plants may transform lime compounds. — The function of plants in aiding in the transformation of one lime compound into another suggests itself by the fact that lime is taken up abundantly by common sorrel from soils in which carbonate of lime is practically absent. When once within the plant, the lime performs the valuable function of neutralizing and removing from the circulation, as insoluble calcium oxalate, some of the oxalic acid, the excessive accumulation of which is toxic even to the plant in which it is produced. This compound in its turn, like calcium acetate and other organic calcium salts, is readily broken up into calcium carbonate in the soil in the course of the normal processes of decay; thus actually tending in a slight degree to correct for other plants the soil conditions which are unfavorable to them, but which in no way inhibit the luxuriant growth of the common sorrel. A study of other plants with this feature in mind will reveal other possibilities of a similar character.

454. Miscellaneous effects of lime on plant diseases. — If lime is applied to acid soils, it creates a condition far

more favorable to development of potato "scab" than that which existed at the outset. This action is, however, by no means confined to lime, since sodium carbonate, barn-

Limed Unlimed Limed Unlimed
Nitrate of soda Sulfate of ammonia

FIG. 41. — RYE UNDER TREATMENT.
All fertilized alike with potash and phosphoric acid. A like amount of nitrogen was used in each case.

yard manure, or other substances which are of an alkaline character have the same effect. For this reason lime should usually be introduced into a crop rotation after, rather than preceding, the potato crop. It is also impor-

tant in all cases that the seed tubers should be treated with corrosive sublimate solution, as proposed by Bolley, or with formalin, in order to destroy any germs of the disease which may be present upon them.

The dry spot of oats has also been recently observed in Europe to occasionally follow the use of lime. A somewhat similar or identical disease, or a possible disturbance of physiological function of oat plants, has been observed on silt loam soil in occasional years at the agricultural experiment station of the Rhode Island State College. The evidence thus far at hand points rather to a disturbance of physiological functions. It is notable that the difficulty seems to depend, nevertheless, in a great measure upon the prevailing climatic conditions, for in certain seasons no injury has been observed.

It was thought at first in Europe that the difficulty was confined to the moor (peat) soils, but it is now recognized as occurring also on sandy and clayey soils; and Hudig[1] believes it to be due to changes in the composition of the humus brought about by repeated applications of the lime, or by other physiologically alkaline fertilizers.

The use of excessive amounts of lime or of other alkaline substances has been found to encourage a disease of tobacco known as "tobacco root rot"[2] which is caused directly by a fungus (*Thielavia basicola*), the development of which may be hindered by the use of acidic fertilizers. It has been suggested also that similar treatment may aid in combating certain diseases of the ginseng.

A striking illustration of the lessening of disease by the use of lime is afforded by the "club-foot," "aubury," or

[1] E. S. R., *25*, 724; also Landw. Jahrb., *40* (1911), 613–644.

[2] Circ. No. 7, Bureau of Plant Industry, U. S. Dept. of Agr. (1908) by Lyman J. Briggs.

Air-slaked lime

Unlimed

FIG. 42. — TREATMENT FOR POTATO SCAB.
Complete fertilizer in both cases.

Calcium sulfate

Calcium chlorid

FIG. 43. — TREATMENT FOR POTATO SCAB.
Complete fertilizer in both cases.

" finger-and-toe " disease of the cabbage, turnip, and other related plants of the *Cruciferæ* family. This is accomplished by the employment of especially heavy applications of caustic lime immediately following a badly diseased crop, and again just before the growing of crops subject to the disease.

455. Lime in connection with potato scab. — The effect of lime in encouraging potato scab has been mentioned briefly elsewhere, but the subject is of such importance that it requires more than passing notice.

Earlier ideas. — Prior to the year 1891 when Thaxter [1] discovered that potato scab was caused by a fungus (*Oöspora scabies* Thaxt.), many observations had been made in Germany and elsewhere upon its appearance. Its occurrence had previously been attributed to lime and to many other substances, on the ground that they caused an irritation or injury to the surface of the tuber, and that in the attempt to recover from the injury the characteristic growth of scab devleoped.

The work of Thaxter. — The laboratory investigations of Thaxter were supplemented by him by field trials of various substances for one season, in the course of which he found 60 per cent of scab when broken plaster and cement were used in the hill, whereas in alternate hills in which mixed fertilizer was used but 6 per cent of scab was found. Among other materials Thaxter also employed wood-ashes in the same manner as the broken plaster and cement. In this case but 7.5 per cent of scab resulted, whereas in the alternate hills without wood-ashes but with the mixed fertilizer 12.5 per cent of scab was observed. From the foregoing it is obvious that the results furnished no conclusive evidence of lime having promoted the devel-

[1] An. Rpt. Conn. Agr. Expt. Sta. (New Haven), 153–160.

Calcium carbonate

Calcium oxalate

FIG. 44. — TREATMENT FOR POTATO SCAB.
Complete fertilizer in both cases.

Calcium acetate

Wood-ashes

FIG. 45. — TREATMENT FOR POTATO SCAB.
Complete fertilizer in both cases.

opment of scab, since they were negative with wood-ashes, which doubtless supplied much more carbonate of lime than was present in the broken plaster and cement.

The work at the Rhode Island experiment station. — Upon the conclusion of Thaxter's work the matter was carefully investigated for a period of four years at the experiment station of the then Rhode Island College of Agriculture and Mechanic Arts [1] with the result that slaked lime, wood-ashes, calcium carbonate, calcium oxalate, calcium acetate, sodium carbonate, and barn-yard manure were all found to encourage the development of potato scab to a most serious extent, in case the causative fungus was present on the "seed" tubers or was already existent in the soil. On the other hand, calcium sulfate, calcium chlorid, sodium chlorid, and oxalic acid either failed to increase the scab or materially lessened it. By the use of a complete fertilizer, even with badly scabbed "seed" tubers, little or no scab ensued on soil which was quite acid. It was conclusively shown, also, in cases in which the soil was already badly contaminated by the fungus, and where it had been made favorable to potato scab by the use of alkaline manures or amendments, that treatment of the "seed" tubers exerted no appreciable protective influence against scab.

Owing to the fact that in Thaxter's laboratory experiments the fungus failed to thrive well, not only on very acid, but also on very alkaline, media, it seems likely that the reason the wood-ashes failed to encourage scab, in his original field experiment, was that they were probably employed at rates far in excess of what would be usually applied to land, thus creating a strongly alkaline reaction, which may be just as protective against scab

[1] Bulletins 26 (1893), 30 (1894), 33, (1895), and 40 (1896).

as a condition of extreme acidity. This explains also the reason why broken plaster and cement should have encouraged scab, for the active lime therein must have been relatively too small to produce such a degree of alkalinity as would have been produced by the combined action of the carbonates of lime, magnesia, potash, and soda, all of which may have been present in the wood-ashes.

456. Lime may be used and potato scab avoided. — Notwithstanding the tendency of lime to promote potato scab, it has been used periodically at the experiment station of the Rhode Island State College in several crop rotations in quantities amounting in the aggregate to about 3200 pounds of calcium oxid in a period of about twenty years, and yet without practical injury to the potato crops from scab. In this case, however, the lime is applied in the rotations immediately following the potato crops, at intervals of from three to six years, and the tubers are always treated with formalin or with corrosive sublimate solution before they are planted. The importance of these precautions is obvious, in view of the fact that in certain of the experiments in Rhode Island, in which they were not taken, the scab fungus has survived saprophytically an interval of seventeen years without an intervening potato crop.

457. Lime may cause injury to pineapples. — It has been reported by Gile[1] that when lime is present in sandy soils, in excess, it may be a cause of pineapple chlorosis. In such cases treatment of the leaves and soils with iron salts, though said not to be feasible from an economic standpoint, proved to be an effective antidote. The treatment of the leaves is in accord with recent experi-

[1] Porto Rico Agr. Expt. Sta., Bul. 11.

ments showing that inorganic fertilizers can enter plants effectively through the leaf.

458. The effect of lime on the size of potatoes. — Many

Limed Unlimed Limed Unlimed
Nitrate of soda Sulfate of ammonia

FIG. 46. — OATS UNDER TREATMENT.

All fertilized alike with potash and phosphoric acid. A like amount of nitrogen was used in each case.

experiments on an acid silt loam at the agricultural experiment station in Rhode Island, covering several years, have shown that liming frequently results in increasing the total crops of potatoes. This effect is, however, in-

consequential compared with the great increase in the relative per cent of large tubers, a point which is of decided economic importance.

459. Liming may hasten crop maturity. — The question of the influence of lime in hastening crop maturity has been much debated pro and con, probably for the reason that its effects are very different, depending upon the character of the soil, the crop, and other attendant conditions.

If the physical condition of a soil were injured by liming, the growth of crops might be unduly prolonged; but if liming were to improve the physical condition, it would be expected that the maturity of the crops grown upon the soil would be hastened.

If there were a lack in the soil of readily available nitrogen, phosphoric acid, or potash, at the outset, to meet fully the plant requirements, the tendency would be to delay growth, and hence the final maturity of the crop. If, on the other hand, liming were to promote a sufficiently active ammonification and nitrification, or if it were to bring about a sufficient liberation of lacking mineral ingredients to meet the complete needs of the plant, without material excesses, growth would follow rapidly from the outset, and maturity would probably be hastened.

If a soil were very acid, and hence poorly adapted to the luxuriant growth of certain plants, liming would likewise be expected to hasten development and maturity. In this way one may account for the marked increase in large potato tubers mentioned previously. For similar reasons crops of onions have been observed to ripen from two to three weeks earlier on land which had been limed three times in the course of fifteen years than where the land had been limed but twice in the same interval. It has been

observed in cases where liming failed, or practically failed, to increase the yield of Indian corn, that the maturity was nevertheless hastened from a week to ten days.

On acid soils the effect of lime in hastening the maturity of cantaloupes and of kohl-rabi has often been found to be very marked.

Limed Unlimed Limed Unlimed
Nitrate of soda Sulfate of ammonia

FIG. 47. — WHEAT UNDER TREATMENT.

All fertilized alike with potash and phosphoric acid. A like amount of nitrogen was used in each case.

In case a soil were already abundantly supplied with all needed forms of plant food, and large quantities of nitrates were to be produced, as a result of liming, this additional supply would naturally have a tendency to prolong growth at the expense of maturity, just as was found by Voorhees to be the case when repeated applications of nitrate of soda

were made to tomato plants, in contrast to a single application at the outset.

460. Soils needing liming for some plants ideally adapted to others. — Soils giving strong and quick re-

Limed Unlimed Limed Unlimed
Nitrate of soda Sulfate of ammonia

FIG. 48. — BARLEY UNDER TREATMENT.

All fertilized alike with potash and phosphoric acid. A like amount of nitrogen was used in each case. Comparisons with Figs. 41, 46, and 47 show that barley is more helped by liming than wheat, oats, or rye.

actions with blue litmus paper and with ammonium hydroxid are frequently highly toxic to certain very sensitive plants, even though the soils have not been fertilized at all for many years with either chemical fertilizers or barn-yard manure other than perhaps the occasional

dropping of dung by horses or cows. It is not to be supposed that the ill effect upon certain plants is necessarily due in all cases directly to soil acidity, but perhaps chiefly in many cases to toxic iron compounds, toxic organic substances, or other deleterious compounds accompanying the lack of basic substances, or arising in consequence thereof, which are oxidized, catalysized, or otherwise destroyed as a result of the application of lime.

461. Details concerning the lime requirements of different plants. — It is not safe in any event to generalize from experimental results secured with one, or even with several, plants in regard to the lime requirements of other plants in their relation to the soil. This is well illustrated by the fact that a soil rendered so toxic by the long-continued application of ammonium sulfate as to absolutely inhibit the growth of the poppy, lettuce, beet, cantaloupe, asparagus, cress, onion, barley, clover, and a whole series of other agricultural and ornamental plants will yet produce better plants of the common sorrel, cranberry, or *Silene orientalis* than it will after the condition, so highly unfavorable to most plants, had been corrected by liming. With only the latter plants in mind, and provided one had not experimented with others, the natural assumption might be that agricultural soils are never so acid or so charged with toxic substances as to interfere with the growth of plants, for the worse the condition becomes for certain plants, within reasonable limits, the better certain others seem to thrive. Similarly, on the other hand, certain plants are best suited by conditions of alkalinity or salinity which are totally destructive to the great majority of agricultural plants.

On account of a lack of sufficient appreciation of these conditions, the agricultural press and even scientific pub-

lications often contain statements to the effect that legumes are in great need of liming, in order that they may develop root nodules and properly assimilate atmospheric nitrogen. Nevertheless, the Southern cowpea, serradella, and certain of the lupines are likely to be injured by heavy liming. Other legumes may possibly be injured under the same conditions, whereas the alfalfa and winter vetch suffer seriously, for lack of lime, even where clover will still grow with moderate success.

Not only the lupines (*Lupinus*), but also the beans (*Phaseolus*), differ widely among themselves as to their requirements for lime in its amendatory capacity.

CHAPTER XXI

GYPSUM AND WASTE LIME FROM INDUSTRIES

RECENTLY gypsum has been employed in the United States to a smaller extent than formerly, whereas the use of ground limestone, burned lime, slaked lime, and waste lime from certain industries has increased.

462. Early use of gypsum. — Gypsum (land plaster or calcium sulfate) has been used as a fertilizer since the time of the earliest Greek and Roman writers. Much mystery surrounded its action in earlier times, which has been removed by modern discoveries in agricultural science. It is now available as ground gypsum and as a by-product of the manufacture of double superphosphate.

463. The source of some of the gypsum in soils. — In certain localities considerable calcium sulfate is present in soils naturally, and since the advent of superphosphates it has been added in that form to the land in considerable quantities, with but little thought on the part of the user that it was present in the usual commercial fertilizer which he was applying.

Gypsum has also been added to soils incidentally, in some cases, in kainit, which is used by itself or as a frequent constituent of ready mixed commercial fertilizers.

The effect of gypsum and lime on clover and other plants. — In Europe, generally, gypsum has long been considered as a specific for clover; and in many cases it has been found to give much better results than lime. Indeed,

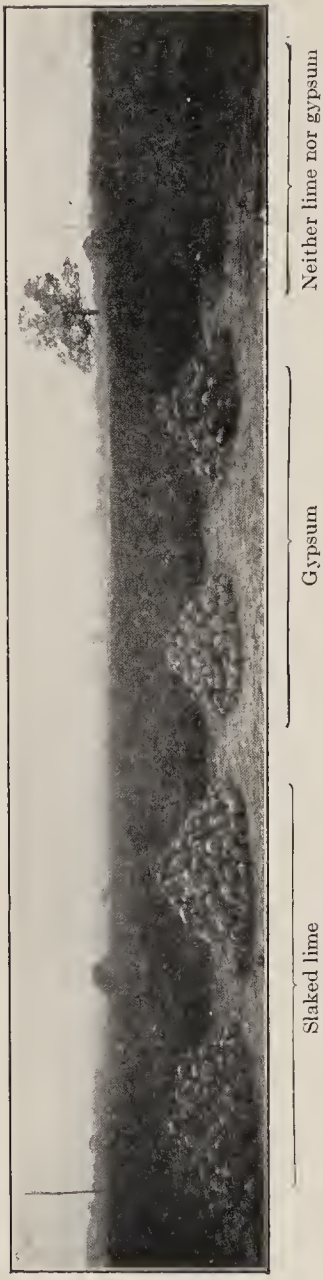


FIG. 49. — TABLE BEETS UNDER VARIED TREATMENT.
The slaked lime and gypsum each supplied like amounts of calcium oxid. All fertilized with like amounts of potash, phosphoric acid, and nitrogen.

Storer [1] cites several such cases and mentions in the same connection that Gasparin found it to work well on a soil containing 20 per cent and more of lime.

In experiments at the agricultural experiment station of the Rhode Island State College it was found, on an acid silt loam soil, that, notwithstanding a striking gain in beets and clover resulting from the use of gypsum, the employment of the same quantity of calcium oxid in air-slaked lime gave far better results.

In order to throw light upon other similar discrepancies in the use of these substances, it should be pointed out that Gasparin was dealing with a soil well supplied with lime, in which the general conditions were not unfavorable to the growth of the particular crop concerned, whereas in the experiment made in

[1] Agriculture, etc., Vol. 1 (1897), 326.

Rhode Island the soil was a silt loam essentially devoid of carbonate of lime and so deficient in bases as to quickly and intensely redden blue litmus paper and to yield large quantities of humus ("matière noire" of Grandeau) upon extraction with dilute ammonium hydroxid, without previous extraction with hydrochloric acid. It was also shown that applications of sodium carbonate, potassium carbonate, and burned magnesia very largely corrected the condition of this soil for beets and other plants, but that the corresponding sulfates were of little or no avail. It is evident, therefore, that in Gasparin's experiment neutralization of the soil was not needed, and gypsum was helpful probably chiefly because of the liberation of potash or possibly by virtue of supplying sulfur, both of which clover greatly needs. Gypsum may nevertheless also have been useful in liberating magnesia and phosphoric acid or in counteracting an improper relation between lime and magnesia, if such existed.

The possibility of some indirect action in the experiment by Gasparin is well illustrated by experiments by Boussingault in which the application of gypsum resulted in raising very greatly, not only the percentage of lime in clover, but also the content of potash, magnesia, phosphoric acid, and sulfuric acid.

In the Rhode Island experiment generous applications of complete fertilizer were made in both cases, which would naturally have lessened any benefit arising from the possible liberation of plant food ingredients of the soil.

464. Gypsum poorer than lime on acid soils. — The chief factor causing the superior action of the slaked lime in Rhode Island was the fact that the prime difficulty with the soil was its acidity, which the lime could neutralize at

once, but which the gypsum could correct but little, if at all, until by possible processes of reduction some of the sulfate had been transformed into calcium sulfid and this in turn into calcium carbonate through the action of carbonic acid.

465. Gypsum may yield calcium carbonate in the soil. — The formation of calcium carbonate from gypsum is indicated by the following equations: —

(1) $CaSO_4 + 2\,C = 2\,CO_2 + CaS$

calcium sulfate — carbon — carbon dioxid — calcium sulfid

(2) $CaS + CO_2 + H_2O = CaCO_3 + H_2S$ (volatile)

calcium sulfid — carbon dioxid — water — calcium carbonate — hydrogen sulfid

It must be remembered, however, that these changes take place under anaërobic conditions, which are not likely to be vigorously maintained for a great length of time in fairly open, well-drained soil which is in good tilth.

466. Gypsum may furnish lime or sulfur as plant food. — It is possible that cases may occur where gypsum is useful by virtue of supplying either lime or sulfur to the plant, in the capacity of a plant food ingredient, but in general the explanation is more properly to be sought in an indirect manurial action, by virtue of the liberation of other plant food elements.

467. Factors determining the choice between gypsum and lime. — When dealing with soils which are acid and with plants readily subject to injury by such acidity or by the toxic substances which often accompany it, either slaked lime or calcium carbonate is likely to prove more effective as a soil amendment than gypsum. In the case, however, of nearly neutral, neutral, or alkaline soils, or of

plants that find therein optimum conditions, as concerns their chemical reaction, it is probable that gypsum will be found to act better than the other compounds of lime.

468. Gypsum as a retainer of ammonia. — Whereas much weight was formerly attached to gypsum as an agent for changing the ammonia of ammonium carbonate into ammonium sulfate, whereby its volatilization might be avoided, it has been found that much moisture is necessary to the change, and furthermore the reaction is only partial and even then reversible, so that the importance of gypsum in this connection, under many of the conditions practically to be dealt with, seems to have been much overestimated.

469. Methods of applying gypsum. — For clover it has generally been found to be a good practice to apply the gypsum to the moist leaves when the plants are only a few inches high. Similarly, it has been applied with good results to potatoes by scattering it along the top of the drill after the plants are well up and immediately before cultivating them. It may of course be spread broadcast, and then be harrowed into the soil, especially before seeding to clover and before the planting of other crops.

470. Gypsum as an oxidizing agent. — Mention has been made of the reduction of calcium sulfate to calcium sulfid, and it should be recognized that in connection with this process gypsum plays the rôle of an oxidizing agent. It furnishes the oxygen for the destruction of the vegetable matter, which takes place through the intervention of the microörganisms of the soil.

471. Gypsum may sometimes aid nitri cation. — Owing to the capacity of gypsum to react with ammonium carbonate to form ammonium sulfate and calcium carbonate, it has been shown by Warrington to be effective

in promoting nitrification in liquid manure or in manure heaps, where the reaction is too alkaline at the outset for nitrification to begin.

472. Gypsum a renovator of alkaline soils. — Gypsum has been shown by Hilgard and others to be an efficient substance for counteracting black alkali (sodium carbonate) in consequence of its reacting with it to produce sodium sulfate and calcium carbonate, whereby the alkalinity is greatly reduced.

473. Effect of gypsum on the solubility of lime. — It has been shown by Cameron and Bell [1] that the solubility of gypsum is depressed in an increasing degree as the amount of lime (CaO) in the solution is increased, whereas with increasing amounts of gypsum in the solution the solubility of lime seems to be nearly the same as in pure water.

474. Gas-lime and lime from other industries. — "Gas-lime," or "gas-house lime" as it is sometimes called, should lie exposed to the air for some time in order to effect the destruction of certain poisonous substances, before it can be applied to the land with safety. The lime in the processes of purifying the gas is changed very largely into calcium sulfate, and hence it cannot perform the same functions as slaked lime, burned lime, or calcium carbonate.

The lime waste from acetylene lighting plants is essentially hydrated lime, and it has been used agriculturally with good results. The same is true of the waste lime from beet-sugar factories and from other industrial works.

It is always a wise precaution to have waste factory products examined by an agricultural experiment station

[1] Jour. Am. Chem. Soc., *28* (1906), 1220; Bul. No. 33, Bur. of Soils, U. S. Dept. of Agr. (1906); Jour. Phys. Chem., *11* (1907), 273.

before attempting to utilize them for manurial purposes, for the reason that factory processes are subject to frequent changes, and the presence of some one or more substances toxic to plant life is not unusual in the residues from certain industries.

CHAPTER XXII

MAGNESIA AS A FERTILIZER

In 1851 E. von Wolff [1] pointed out the beneficial effect of magnesia upon plant growth, although Mulder believed it was merely due to its liberation of other plant foods.

475. Functions of magnesia in the plant. — It was shown by the work of Schmiedenberg [2] that magnesia was possibly of importance in connection with the formation of the albuminoids. At present, however, magnesia is not believed to play a direct rôle in connection with protein formation.

According to E. von Raumer [3] magnesia performs useful functions in connection with the translocation of starch, though in this respect potassium is now known to be particularly important.

It has been asserted by Loew and by Hilgard [4] that magnesia serves in the plant as a carrier of phosphorus, where, according to Hilgard, it exists as dimagnesic-hydric phosphate. The fact that more magnesia is present in oily than in starchy seeds, supports this view, since lecithin, which is rich in phosphorus, is formed in cells rich in oil. It is furthermore stated by Reed that there

[1] Erdmann's Jour., *51* (1851), 15.
[2] Zeits. f. Physiolog. Chem., *1*, 205.
[3] Die landw. Vers.-Sta., *29*, 279.
[4] Soils, etc. (1906), 382.

is often a very definite relation between the magnesia and the vegetable oils. It is also of interest to note that Ville found, when magnesia was omitted, that the yield of wheat fell from 337 to 123 grains.

According to Bretfield [1] an increase in the dry weight of plants is impossible in the absence of magnesia. In experiments by Dassonville,[2] with magnesium sulfate,

No lime Ground magnesian limestone Slaked Lime

FIG. 50. — ALFALFA ON FARM.

All fertilized alike with potash and phosphoric acid. Quantities of lime having the same total neutralizing value were used in each case.

it was found that, though delaying the growth of certain legumes at the outset, it became finally indispensable. The participation of magnesia in some of the most important synthetic processes of the plant is asserted by Strasburger, Noll, Schenck, and Schimper.[3]

In brief, no one now questions that magnesia is essential to plant growth.

476. Conflicting ideas as to the action of magnesia. — According to Atterberg,[1] the compounds of humus

[1] Pflanzenphysiologie (1884), 135.

[2] Revue générale de Botanique, *8* (1896), 331; Abs. Jahresb. f. Agr. Chem. (1896), 260.

[3] A Textbook of Botany, translated by Porter (1898), 173.

with lime are less soluble than those of humus and magnesia.

It was asserted by Stutzer [2] as late as 1893 that soils usually contain sufficient magnesia to meet plant requirements, yet D. Meyer,[3] for example, attaches special value

FIG. 51. — TREATMENT OF OATS.

1. Unlimed. 2. Calcium chlorid in 1894 and 1895. 3. Same as 2, with addition of caustic magnesia in 1897. 4. Same as 2, with addition of slaked lime in 1897. All fertilized alike with complete fertilizer.

to magnesian lime as compared with the high calcium limes, in connection with the growth of certain legumes; and Larbalétrier and Malpeaux report the use of magnesium sulfate as advantageous for beets, for some years, in the Department of Pas-de-Calais, France. Similar results are also recorded by Stöckhardt, in Saxony, and like

[1] Svenska Mooskultur-föreningenstidschrift (1891), 121, 122; Abs. Centralb. f. Agrik. Chem, *21*, (1882), 298, 299.

[2] Leitfaden der Düngerlehre, p. 16.

[3] Landw. Jahrb., *29* (1900), 961.

instances may be cited from experiments in Rhode Island,[1] and elsewhere in the United States.

It has long since been observed that experimenters in different localities have sometimes secured quite opposite results from the use of magnesia, as, for example, in the case of the good results secured by Ville when it was used for wheat and the ill effect on wheat noted by Passarini.[2]

It has been pointed out by Storer that Tennant noted a poisonous action of caustic magnesia, yet in recent experiments at the Maryland experiment station caustic magnesia at the rate of 1400 pounds per acre gave in certain instances better results than the same amount of calcium oxid in ground oyster shells. In fact, many similar conflicting instances might be cited.

It has been stated that Von Raumer, in 1883, pointed out the necessity of a proper relationship of lime to magnesia in connection with plant growth; and Knop called attention at an early date to the fact that in water-culture experiments certain calcium, potassium, or ammonium salts were capable of counteracting the ill effects of an excess of magnesia, and he suggested the applicability of lime as an antidote for magnesia in field culture. Many other investigators have found lime an antidote for an excess of magnesia in field practice. Later, a theory was advanced by Loew[3] which may explain, in many cases, this interesting and important fact.

477. Loew's theory concerning magnesia. — In brief, Loew holds "that a calcium protein compound partici-

[1] An. Rpt. R. I. Agr. Expt. Sta., *17* (1903–1904), 230–234.

[2] Bol. Scuolo Agr., *3* (1895), 140–142; Abs. Jour. Chem. Soc. (London), *72*, No. 142, II, 587.

[3] Die landw. Vers.-Sta., *41*, 466–475; also Flora (1892), 368–394; Bul. 18, U. S. Dept. of Agr., Div. of Veg. Phys. and Path. (1889), 42.

FIG. 52. — CLOVER, REDTOP, AND TIMOTHY, PROMINENT IN THE ORDER NAMED.
Hydrated lime containing a small amount of magnesia. "Complete" fertilizer. Seeded to timothy, redtop, and clover, the same as in Figs. 53, 54, and 55.

pates in the organized parts of the nucleus and chlorophyl body," and that when magnesium salts of the stronger acids are made available to the plant, the lime as the stronger base would "combine with the acid of the magnesium salt, while the magnesia would enter into the place which the lime had occupied in the organized structure; the capacity for imbibition would thereby be altered and a disturbance of its structure would result which would prove fatal.

"On the other hand, judging from the laws of the action of masses, it would naturally be inferred that an excess of lime salts would remedy the evil effects by making the reverse

process possible." It is not to be assumed, however, that all cases of injury arising from the use of magnesia are due to the reason given by Loew and his various coworkers, for other factors often come into play. It appears probable, nevertheless, that there are certain fairly definite relations between lime and magnesia which are best for given kinds of plants, and yet for other plants they may be widely different. The recent work by Gile shows that in some cases the importance of the very close and definite relationship may have been overestimated. The investigation of this question is, however, yet in its infancy.

There has unquestionably been too great a tendency to explain cases of injury arising from the use of magnesium salts on the basis of Loew's theory, for in many cases some other explanation harmonizes far better with the observed facts.[1] These attempts to support the theory of Loew by frequent unwarranted claims have resulted in awakening unnecessary fear of magnesia poisoning, even in regions where magnesia is not present in soils in undue proportions as compared with lime, and where its application is often followed by good results.

478. The ratios of lime and magnesia in different soils. — It has been asserted by D. Meyer [2] that soils with an especially high content of magnesia, as compared with the lime, are quite exceptional; yet Loew [3] cites analyses of twenty soils from different parts of Japan in which the magnesia exceeds the lime by from two to five times, and the relations of the two in the soils of Japan have been found to range from traces of lime associated with 0.475

[1] An. Rpt. R. I. Agr. Expt. Sta., *17* (1903–1904), 221–260.
[2] Landw. Jahrb. (1904), Heft 3.
[3] *Ibid.* (1905), 133.

per cent of magnesia to such limits as 1.618 per cent of lime and 6.307 per cent of magnesia. Other analyses of Japanese soils are also cited in which quite the opposite relation was found to exist.

Magnesia has also been found in excess of the lime in certain of the soils of Ohio, which have been greatly helped by liming, yet the benefit in this case may well be due chiefly to other effects than the correction of an unfavorable ratio between lime and magnesia. Indeed,

FIG. 53. — CLOVER, REDTOP, AND TIMOTHY, PROMINENT IN THE ORDER NAMED.

Hydrated magnesian lime with high magnesia content. "Complete" fertilizer. Seeded to timothy, redtop, and clover, the same as in Figs. 52, 54, and 55.

even Loew (*ibid.*, p. 135) calls attention to the neutralizing value of both calcium carbonate and magnesium carbonate, and to their frequent beneficial action, in this capacity, upon the bacterial flora of the soil, which effects, he admits, may in certain cases be so great as to obscure the physiological effects due to correction of the calcium-magnesium ratio. He also adds that otherwise in soils containing about equal quantities of lime and magnesia the yield of cereals would be depressed by an application of either.

In order to arrive at the lime and magnesia available

in the soil, Loew prefers an extraction of the fine earth with 10 per cent hydrochloric acid rather than with a 10 per cent solution of ammonium chlorid, which was employed by Meyer.

479. Variations in magnesia content of different parts of the same plant. — Instances are cited by Loew [1] of certain seeds in which there are found one hundred molecules of magnesia to seventeen of lime, and yet in the leaves there were two hundred and twenty-four molecules of lime to one hundred of magnesia.

480. Concerning the alleged toxic action of magnesium chlorid. — It was suggested by Knop that in certain soils sulfate of potash should be employed rather than muriate of potash on account of the possibility that magnesium chlorid might otherwise be formed, which Knop regarded apparently as a positive plant poison.

According to the theory of Loew, magnesium chlorid would be expected to have a toxic action upon plants, at least whenever the lime was deficient. In fact, he states [2] that "calcium and magnesium chlorid have an injurious effect upon plants, probably on account of the liberation of hydrochloric acid in cells, this not being assimilated like nitric and sulfuric acid and therefore accumulating to a noxious degree."

It has been stated by L. von Wagner [3] that calcium and magnesium chlorids are not good for potatoes and beets.

It is obvious that excessive amounts of magnesium chlorid, like other salts, must inevitably be injurious to plant life; the degree of injury depending upon the kind of plant and the concentration of the salt solution.

[1] Die landw. Vers.-Sta., *41* (1892), 473.

[2] Bul. 18, U. S. Dept. of Agr., Div. of Plant Phys. and Path., 18.

[3] Pflanzen-Produktions-Lehre (1874), 336.

A study of the effect of magnesium chlorid was made by Wheeler and Hartwell [1] on a silt loam containing about 0.57 and 0.21 per cent, respectively, of lime and magnesia soluble in strong hydrochloric acid, as determined by the Hilgard method of soil analysis. The land had been planted to Indian corn for several years, without fertilizer or manures, until it would no longer produce a crop over 6 inches high in the course of a whole season. The experiments were made in galvanized iron pots 18 inches in diameter and 26 inches deep, with the bottoms sloping to an opening in the center. The pots were set in soil nearly to their tops over drain tile, which insured normal conditions of temperature and prevented the backing up of water into them from the surrounding soil. The first two years all of the pots received acid phosphate, nitrate of soda, and muriate of potash, and the third year dried blood, basic slag meal, and potassium-magnesium carbonate (a product of the German potash works). The average yield of barley plants per pot the first year, without further treatment, was 43.7 grams, and upon the addition of 19.2 grams of hydrous magnesium chlorid per pot the yield was 46.5 grams. By the use of 110 grams of calcium carbonate per pot in addition to the magnesium chlorid the average yield was raised to 67.9 grams; but when caustic magnesia was added at the rate of 44 grams per pot in place of the calcium carbonate, the average yield fell to 6.1 grams.

The following year the application of magnesium chlorid was repeated, and spring rye was grown. The average yield with magnesium chlorid was 51.3 grams; the yield where calcium carbonate had also been applied, the previous year, was 55.8 grams; and where caustic magnesia

[1] An. Rpt., R. I. Agr. Expt. Sta., *15* (1901–1902), 295–304.

replaced the calcium carbonate, the yield was now 49.7 grams. The toxic action of the caustic magnesia, observed the first year, had now practically vanished. It was found that the addition of magnesium carbonate at the rate of 59.2 grams per pot, where the caustic magnesia had been applied the year before, resulted in a depression of the yield to 41.4 grams. This second year the check pots to which no magnesia had been added in any form gave an average yield of but 3.7 grams.

The third year the crop was oats, and the average yield with magnesium chlorid was 84.4 grams of oat plants per pot. Where calcium carbonate had been added two years before, the average yield was now 79.4 grams; that where caustic magnesia was used two years before was 87.9 grams; and the yield where caustic magnesia was used two years before, and magnesium carbonate a year before, was 82.5 grams. It is of special interest to note that the yield of the check pots as a result of using a basic magnesian fertilizer was now 88.7 grams. The magnesium chlorid had not in this case proved materially or positively toxic, since the differences are within the reasonable limit of error. In view of the improvement in yield from the use of calcium carbonate and the injury from caustic magnesia the first year, it might have been assumed, on the basis of Loew's theory, that the lime had been helpful by virtue of counteracting an undue proportion of magnesia; yet such a conclusion is impossible in view of the excellent results in every case in the last year, where magnesium salts were used as additions to the magnesium chlorid and the regular fertilizer. It has since been shown by field experiments that this soil had finally become so acid as to inhibit almost absolutely the

growth of timothy, clover, and barley, until the condition was corrected by the addition of calcium carbonate, potassium-magnesium carbonate, burned dolomite or slaked lime (slightly magnesian). This fact accounts for the poor results of the second year in the check pots when muriate of potash and acid phosphate were used, and also for the toxic action of ammonium chlorid when used in an experiment under the same conditions as magnesium chlorid. This also explains the effect, the first two years, of calcium carbonate in more than counteracting the tox-

FIG. 54. — REDTOP. (CLOVER AND TIMOTHY LACKING.)
Complete fertilizer. No lime. Seeded to timothy, redtop, and clover, the same as in Figs. 52, 53, and 55.

icity of the ammonium chlorid, and also the effect of the basic fertilizer made up of basic slag meal, dried blood, and potassium-magnesium carbonate, in correcting, in all cases, the conditions in the check pots in the third year.

The foregoing results show that magnesium chlorid is less toxic on certain soils than ammonium chlorid; and still other experiments with the same soil indicate that it is far less toxic than calcium chlorid.

481. Danger from using caustic magnesia and burned and hydrated magnesian lime. — The preceding results show that caustic magnesia was toxic at first when it was used in large quantities, even on a soil evidently in

slight need of magnesia, but that when sufficient opportunity had been afforded for it to become carbonated, it became useful. It is probably on this account that special care must be taken in employing a hydrated, air-slaked, or burned magnesian lime immediately before planting a crop, unless great care is taken to limit the quantity used to moderate applications, and to most thoroughly incorporate it with the soil. Such danger is obviously greater on light, sandy, and gravelly soils, lacking in moisture and vegetable matter, and less on heavier soils rich in vegetable matter, especially if they are of an acidic character.

482. The solubility of magnesium carbonate in its relation to practice and experiment. — According to Comey,[1] magnesium carbonate is more soluble than calcium carbonate in water, carbonated water, and in ammonium chlorid. It has also been shown by Treadwell and Reuter that one liter of water will hold only 0.385 gram of calcium bicarbonate in solution, but that the same amount of water will hold in solution at one time, not only 1.954 grams of magnesium bicarbonate, but also 0.715 gram of magnesium carbonate. For this reason there is much more danger of injury from heavy applications of burned and slaked magnesian lime than from the pure lime, especially on soils but little in need of basic applications, and for plants which are particularly susceptible to such injury as may arise in consequence of the creation of an alkaline reaction in the soil solution. Notwithstanding that these figures may apply to magnesium carbonate, which is formed by the taking up of carbonic acid by slaked magnesian lime, it is doubtless not true of the magnesium carbonate in natural magnesite, dolomite,

[1] A Dictionary of Chemical Solubilities, London and New York, 1896.

or highly magnesian limestone; for Hilgard[1] has pointed out that magnesia in its native combinations leaches less rapidly from soils, than lime, indicating that the relative solubilities of artificial carbonates may be quite the reverse of the natural compounds. In fact, the mineral magnesite (magnesium carbonate) is said to be probably insoluble in water and not to be affected by boiling with water or with aqueous solutions of alkaline carbonates.[2] Experiments conducted under the direction of B. L. Hartwell, at the request of the writer, have also shown that ground magnesian limestone, sufficiently fine to pass a sieve with 50 meshes to the linear inch, was much less soluble in carbonated water maintained in a state of saturation than ground limestone passing a sieve of the same mesh. In fact, the solubility of the latter was approximately three times as great as the solubility of the former.

If, therefore, quick action is necessary, magnesium carbonate, if formed recently from burned magnesian lime, would be expected to correct undue acidity of soils rather more quickly than calcium carbonate; but natural magnesite, dolomite, or magnesian limestone might accomplish it less quickly than natural carbonate of lime.

It has been shown by H. Ley [3] that neutral salts check or prevent dissociation, hence magnesium carbonate as well as calcium carbonate may be expected to act favorably on acid soils in preventing dissociations of compounds possessing ions of a character injurious to plant growth. On the other hand, the high solubility of magnesium

[1] Soils, etc. (1906), 383.

[2] Davis, Jour. Soc. Chem. Ind., *25* (1906), 788; cited from Cameron and Bell, Bul. 49, Bur. of Soils, U. S. Dept. of Agr., 59.

[3] Ber. d. deut. chem. Gesell., *30*, 2192.

carbonate, such as would be likely to be formed quickly from burned magnesian limestone in the soil water, and the possibility of creating by its presence alkaline conditions unfavorable to certain plants, has been very frequently neglected or ignored in farm practice and also in experimental work. In consequence, in certain instances very erroneous conclusions have doubtless been drawn. In fact, no experimenter can afford to neglect the possibility of such effects any more than he should, for example, the possible influence of such compounds upon the ionization of other salts, upon the bacterial life, or upon the physical character of the soil.

483. Ranges in lime and magnesia content of plants without material differences in yield. — It was found by Wheeler and Hartwell in pot experiments with spring rye in which the average yields of rye plants per pot were 50.5 and 51.3 grams, respectively, that in the former case, in which calcium carbonate was employed, the ratio of lime to magnesia was 6.3 to 1; whereas in the second instance, where magnesium chlorid had been applied, the ratio of lime to magnesia was 1.5 to 1. Results with mangels were also secured in connection with which, in addition to the regular fertilizer, caustic magnesia, sodium carbonate, and air-slaked lime were employed. When caustic magnesia was added to the usual fertilizer, the yield was 126.3 grams of air-dried mangel "roots," and the ratio of lime to magnesia was 6.4 to 1; when sodium carbonate was added, the yield was 131.3 grams, and the ratio of lime to magnesia was 1.6 to 1; when slaked lime was used instead of the caustic magnesia or sodium carbonate, the yields in two cases were 148.2 and 132 grams and the ratios of lime and magnesia 4.4 to 1 and 3 to 1, respectively. Without further addition than that of the

regular fertilizer, the yield was 91.3 grams and the ratio of lime to magnesia was 4.2 to 1.

Attention has been called elsewhere to the fact that plants may be physiologically relieved of certain excesses of lime by its crystallizing out within them as insoluble calcium oxalate and in some cases exteriorly as calcium carbonate. The former disposition is impossible in the case of magnesia, because of the solubility of the magnesium oxalate. It must be evident, therefore, that in

FIG. 55. — EXTREME LEFT, REDTOP AND WEEDS. (NO CLOVER NOR TIMOTHY.)

No lime. No fertilizer. Seeded to timothy, redtop, and clover, the same as in Figs. 52, 53, and 54.

any discussion of the ratios of lime and magnesia in plants, the possibility of such storing away of some of the lime in insoluble, and hence in inactive form, must be taken into consideration; yet in the instance here considered, it does not seem probable that this factor could have had much influence on the relation of the two. It appears, therefore, *as concerns the ratios of lime and magnesia within the plant,* that there may be in some cases very wide variations without an accompanying difference in yield.

484. Desirable lime and magnesia ratios in soils and culture solutions. — According to Loew,[1] a relation of 2 of

[1] Circular No. 10 (1909), Porto Rico Agr. Expt. Sta.

lime to 1 of magnesia in soils is to be desired, because it stands between that which is best for cereals, on the one hand, and for the legumes on the other; he points out, however, that the relative availability of the lime and magnesia present in the soil may nevertheless change these ratios materially, a difference not revealed by his chemical method of determining them. Furthermore, these generalizations, especially as to the legumes, may be hasty and subject to material modification, depending upon the individual legume concerned.

It has been established experimentally by Furuta and Katayama[1] that the most advantageous ratio of lime to magnesia is 1 to 1 for rice and oats, 2 to 1 for cabbage, and 3 to 1 for buckwheat. It appears, in other words, in accord with the relatively greater amount of lime in the leaves, and of magnesia in the seeds, that plants with a great leaf surface may require relatively more lime.

It was found by Bernadini and Corso that the best ratio of lime and magnesia for maize was 2 to 1; for oats in water-culture it was 1 to 1; and in soil culture 2 to 1 was permissible; but a depression in yield resulted with a ratio of 3 to 1. It was noted by Takeuchi that a decrease of two-thirds resulted in the growth of oats, when the ratio of lime to magnesia was changed from 1 to 1, to 10 to 1.

The experiments of Aso, Bernadini, and Corso, and likewise of Konowalow, have indicated the proper lime-magnesia ratio for rice, wheat, rye, and barley to be 1 to 1. For onions, Katayama found 2 of lime to 1 of magnesia the best ratio. For leaf production, in the case of mulberry trees, Aso established the ratio of 3 of lime to 1 of magnesia.

[1] Bul. Col. of Agr., Tokyo, 4, Nos. 5 and 6.

For flax, Nakamura gives the proper ratio of lime to magnesia as 1 to 1.

Experiments by Daikuhara[1] with a soil having 0.64 per cent of lime and 1.91 per cent of magnesia indicated that a ratio of 3 of lime to 1 of magnesia is unfavorable to beans, buckwheat, tobacco, and the cereals.

The recent work by Gile gives evidence of frequent wide variations in the lime-magnesia ratios of soils, without unfavorable effects on the plants.

485. Sources of magnesia. — Magnesia is available for fertilizer purposes in several different forms: —

(1) Magnesite, magnesium carbonate ($MgCO_3$), occurs as a native mineral in California, and elsewhere in the United States, and it is found in considerable quantities in Europe. It is said to be insoluble in pure water and to be exceedingly resistant to carbonic acid.

(2) Dolomite is a whitish-opaque calcium-magnesium carbonate containing about 47.6 per cent of magnesium carbonate, the remainder being carbonate of lime.

(3) Magnesian limestone is one in which a part of the calcium carbonate is replaced by magnesium carbonate in proportions ranging from traces of magnesium carbonate to essentially the quantities present in dolomite.

(4) Dou le manure salt (double sulfate of potash and magnesia), also referred to as low-grade sulfate of potash, and kainit. The latter contains magnesium sulfate, and also carries considerable quantities of magnesium chlorid. These salts and kieserit are considered more fully under the chapter on potash salts.

[1] Bul. Expt. Sta., Tokyo, *1*, No. 1 (1905); cited from Loew.

CHAPTER XXIII

SODIUM SALTS

Sodium is present in the air, as sodium chlorid, in the shape of fine powder. This is derived chiefly from the winds which sweep into the air the spray of the ocean and of salt lakes. The winds also carry into the air salt dust of terrestrial origin. The quantity of common salt thus

Full ration sodium carbonate	Full ration potassium carbonate	One-fourth ration sodium carbonate. One-fourth ration potassium carbonate	Full ration sodium carbonate. One-fourth ration potassium carbonate

Fig. 56. — Mangels, Limed.

Fertilized alike with phosphoric acid and nitrogen.

carried inland is sufficient to materially raise the chlorin content of spring and well waters in near proximity to the sea coast.

In addition to this atmospheric source of sodium, it is a prominent constituent of many important and widely distributed minerals and rocks.

486. Mineral sources of sodium salts. — Orthoclase, one of the chief minerals of certain granites, frequently contains from 2 to 6 per cent of soda; oligoclase, also often

present in granite, contains 8 per cent of soda; diorite likewise contains 3 per cent of soda; and certain volcanic rocks contain as much as 6 per cent. Thus these and other sodium-bearing minerals and rocks add, by their disintegration, to the soluble sodium salts of the soil, and hence aid in their distribution throughout all arable soils. It must be borne in mind, however, that in humid regions sodium as chlorid, and also in other combinations, is being continually leached way, whereas, on the contrary, in arid regions the soluble sodium salts often accumulate to such an extent as to inhibit plant growth, or at least the growth of the usual agricultural plants.

487. Black alkali. — Chief among the noxious sodium salts is the so-called "black alkali" (sodium carbonate, Na_2CO_3), which was so named because of the dark color imparted to the otherwise white sodium carbonate, by vegetable decomposition products which it dissolves.

488. Quantities of common salt injurious to crops. — The soluble sodium of soils is present chiefly as chlorid, although it may occur as nitrate, sulfate, carbonate, or silicate. In dry soils quantities of sodium chlorid as great as 1 to 1000 parts of soil are likely to be injurious to plants, though in very wet soils nearly twice that quantity may be endured.

489. The presence of soda in plants. — The presence of soda seems to be practically universal in cultivated plants, though the amounts in different plants vary widely according to the nature of the plant and to the condition under which it is grown. There is also a wide variation in the percentages present in different parts of the same plant. In elevated regions, very remote from the sea, the quantity of soda present in plants is so small that cattle reared

there require much more common salt than those fed on plants grown nearer the sea.

According to Pagnoul,[1] Peligot first pointed out the difference in the action of soda and of potash upon plants. He made analyses of many varieties of plants,[2] and claimed that the ash of most plants, including spinach, contained no soda, although he found it in fodder beets and in species of *Atriplex* and *Chenopodium*. When, later, Bunge[3] called attention to the faulty method of analysis by which much or all of the soda might have been lost, Peligot re-

Full ration common salt | Full ration muriate of potash | One-fourth ration common salt. One-fourth ration muriate of potash | Full ration common salt. One-fourth ration muriate of potash

FIG. 57. — MANGELS, LIMED.

Fertilized alike with phosphoric acid and nitrogen.

peated some of his earlier work,[4] taking special precautions against the loss of soda, and again found soda absent from certain plants.

It was found by Dehérain[5] and Sjollema[6] that potato tubers were free from soda, notwithstanding that sodium

[1] Ann. Agron. (1899), 467.

[2] Compt. rend. (Paris), *2* (1867), 729; and in later issues of the same journal.

[3] Annal. de Chemie et Pharm., *172*, 16.

[4] Compt. rend. (Paris), *76* (1873), 113; Abs. Centralb. f. Agr. Chem., *4* (1873), 222–226.

[5] Ann. Agron., *9* (1883), 511.

[6] Jour. f. Landw. (1899), 309.

salts were present in the manures. It is reported by Pagnoul [1] likewise that potatoes grown in soil which contained soda were themselves free from it, and later he asserted [2] that sodium may be absent if large amounts of potash are used in the manures. He found, however, that oats absorbed soda if there was a deficiency of potash in the manures and fertilizers.

That the use of sodium salts in the manures may increase the quantity of it in some plants is shown by Zöller, who found in the stems of beans 5.1 per cent when soda was so employed, but only 1.36 per cent when it was not. Similar wide variations were found by Wheeler and Hartwell [3] in various crops.

It is reported that Coutejean and Guitteau [4] determined the potash and soda percentages in over six hundred varieties of plants, and large numbers of similar determinations are given by Wolff.[5] It appears that the soda content of plants may therefore vary from mere traces to high percentages. The amount found by Hilgard [6] in the ash of greasewood (*Sarcobattus vermiculatus*) was 40 per cent.

490. Sodium salts as indirect manures. — It was found by Birner and Lucanus [7] that the application of sodium sulfate favored the passage of phosphoric acid into the plant and that it lowered at the same time the percentage of lime. Upon applying potassium chlorid, the ash and

[1] Compt. rend. (Paris), *80* (1875), 1010; Abs. Jahresb. f. Agr. Chem., *18*, 259.

[2] Ann. Agron., *20* (1894), 467–479.

[3] An. Rpt., R. I. Agr. Expt. Sta., *19* (1905–1906), 235–251.

[4] Compt. rend. (Paris), *86* (1878), 1151–1153; Abs. Centralb. f. Agr. Chem. (1879), 259.

[5] Aschen-Analysen.

[6] Jahresb. f. Agr. Chem. (1892), 183.

[7] Landw. Vers.-Sta., *8* (1866), 140.

dry matter of the plants were enriched in magnesia and potash, but became poorer in lime, sulfuric acid, and phosphoric acid; and upon applying sodium chlorid a still more striking change in the same direction ensued. On the other hand, Storer [1] cites Dyer as authority for the statement that common salt seems to be needed to bring out the action of phosphates and nitrates, yet from observations by various experimenters it would appear that there are many conditions under which common salt is

Full ration sodium carbonate | Full ration potassium carbonate | One-fourth ration sodium carbonate. One-fourth ration potassium carbonate | Full ration sodium carbonate . One-fourth ration potassium carbonate

FIG. 58. — FLAT TURNIPS, LIMED.

Fertilized alike with phosphoric acid and nitrogen.

used to check the too rapid formation or assimilation of nitrates. It is apparent, therefore, that the effect produced hinges upon the peculiar conditions which exist in any given case.

It has been shown by various experimenters that upon applying calcium salts to ordinary soils, considerable amounts of potash are often rendered soluble, and the high efficiency of sodium chlorid in this respect, under exaggerated conditions, has been shown by Passarini.[2] Nevertheless, Müntz and Girard hold that if sodium chlorid

[1] Agriculture, II (1897), 595.

[2] Quorta Seine *17*, Dist. 1a–2a; *72*, della Raccolta Generale, 15.

exerts a solvent action upon soil phosphates or upon soil silicates, containing potash, it must be extremely limited. It must, however, be evident that rich potash-bearing zeolites or, possibly, glauconite would be likely to yield more potash than would be freed from feldspars; and they would also yield considerably greater quantities of potash, if rich in that ingredient, than if they were poor in potash at the outset and were already rich in soda, lime, and magnesia.

In the course of experiments with sodium chlorid and with sodium carbonate, at the experiment station of the Rhode Island State College, the serious deficiency of potash which soon developed, in a silt loam soil of granitic origin, indicated, if there had been a liberation of potash from zeolitic or other silicate combinations, that it could neither have been of very great consequence at the outset nor of long duration. In this case generous amounts of readily available phosphoric acid, as well as occasional applications in less available form, were made throughout the course of the experiments, hence it was not a question of liberation of native phosphorus compounds of the soil. Under the circumstances which existed, it was found that on both lightly and moderately limed soil, both sodium compounds showed an unmistakable tendency, in two or three different years and with several different crops, to increase the percentage of phosphorus in the dry matter of the plants.[1]

491. Concerning the benefit to crops from applying sodium salts. — The old and modern writers on agricultural chemistry and on general agriculture agree that marked benefit to farm crops often follows the application of sodium salts, though reference is commonly made to

[1] An. Rpt., R. I. Agr. Expt. Sta., *19* (1905–1906), 194–219.

sodium chlorid. Recently Smets and Schreiber [1] have pointed out that sodium salts are highly beneficial to certain plants under given conditions of field culture. Frequent ill effects from such use of sodium chlorid are nevertheless on record.

It is apparent that sodium salts act more beneficially with some classes of plants than with others. From this it must be inferred that the different plants require unlike amounts of potash, which soda can liberate, that they are

Full ration common salt	Full ration muriate of potash	One-fourth ration common salt. One-fourth ration muriate of potash	Full ration common salt. One-fourth ration muriate of potash

FIG. 59. — FLAT TURNIPS, LIMED.

Fertilized alike with phosphoric acid and nitrogen.

unequally affected by such biological and physical changes in the soil as the use of soda may cause, or one is led to conclude that soda probably performs functions of direct physiological importance.

The general recognition in Great Britain of the benefit from the application of common salt to soils is evident from the statement by Griffiths [2] to the effect that 250,000 tons of finely crushed common salt are used annually for manurial purposes in the United Kingdom.

In soils which contain calcium carbonate, it is possible

[1] Récherchés sur les Engrais Potassiques et Sodiques, Maaseyck (1896).

[2] A Treatise on Manures (1889), 256.

that common salt, by its reaction with sodium chlorid, may give rise to sodium bicarbonate, which, being more basic than the carbonate of lime, may affect the chemical reaction of the soil either favorably or unfavorably according to the variety of plant involved. It has even been asserted that it may, by its solvent action, render certain humous bodies of the soil either directly assimilable by plants, or else aid in the more rapid change of some of their constituents into other available forms of plant food ingredients. It was found by Prianischnikov,[1] when using sodium nitrate as a source of nitrogen in the growth of plants, that the medium in which they grew became alkaline by virtue of the sodium carbonate which resulted after the removal and utilization of the nitric acid by the plants. Indeed, this is in full accord with later observation of others and with the earlier classification of sodium nitrate, by Adolf Mayer, as a physiologically alkaline fertilizer.

492. The effect of sodium salts dependent on various conditions. — That an excess of sodium carbonate in soils may be injurious, is well attested by the evil effect of the "black alkali" (sodium carbonate) of the arid and semi-arid regions of Canada, the western part of the United States, and elsewhere. If sodium chlorid is used on an acid soil, practically devoid of carbonates of lime and magnesia, it may aggravate the existing condition by ultimately increasing the acidity, whereas on a soil where the sodium chlorid can react with carbonate of lime to form sodium bicarbonate, the reverse effect might follow.

493. The influence of sodium salts on the conservation and movement of soil moisture. — It has been shown by Ricôme[2] in experiments with *Malcolinia maritima* and

[1] Chem. Ztg., *66* (1900), 701.

[2] Compt. rend., *137* (Paris, 1903), 141; Abs. Centralb. f. Agr. Chem., *33* (1904), 224.

Alyssum maratinum that the presence of sodium chlorid in the solution outside of the plant may lessen the quantity of water absorbed, and thus protect it from an injurious degree of transpiration. The presence of the sodium salt in the plant itself was without beneficial effect in this connection, unless the existing conditions were also such as to permit of easier absorption.

Since soluble salts, such as sodium chlorid, increase the surface tension of liquids, it has been pointed out by King that they may be helpful by facilitating the movement of

Full ration common salt | Full ration muriate of potash | One-fourth ration common salt. One-fourth ration muriate of potash | Full ration common salt. One-fourth ration muriate of potash

FIG. 60. — CHICORY, LIMED.

Fertilized alike with phosphoric acid and nitrogen.

the soil water towards the surface, and hence towards the plant roots.

In certain soils sodium chlorid exerts a beneficial flocculating influence, yet in others in which the bicarbonate is readily formed, it may have the opposite effect.

It is generally held by farmers that common salt added to a soil helps it to retain moisture, on which account it is helpful on light sandy soils which are readily subject to drought. This view is supported by the fact [1] that the presence of salts in the soil solution lessens evaporation from the surface so long as they remain in solution, and

[1] King, A Textbook of the Physics of Agriculture (1901), 106.

in case they are separated at the surface, they then even serve the purpose of a mulch.

494. The effect of sodium salts upon osmotic pressure. — There appears to be evidence that conditions may arise in which sodium salts, or other soluble salts, may be of service in connection with the growth of plants in solutions, merely by their increase of the osmotic pressure, though whether this would have any bearing upon the growth of plants in a normal way in soils is problematical.

495. The possible physiological and manurial functions of sodium salts. — Some writers attribute to potassium but the one function of aiding in the formation and translocation of starch, though Benecke [1] indicates others, for in discussing sodium he suggests its osmotic service to the plant as a substitute for potassium. As concerns potassium salts, in this connection, Copeland [2] has asserted that they are direct or indirect factors in maintaining turgor, also that upon the omission of salts containing phosphorus, magnesium, or sulfur, the plants, though showing poor growth, exhibited high turgor, whereas in the absence of potassium salts, the turgor was decreased and the growth stunted. Nevertheless, Pfeffer [3] holds that turgor is a result of conditions of growth rather than a cause of it; a view which seems to have the greater support.

It is held by Pfeffer that phosphorus may be as essential as potassium in effecting the formation and translocation of starch; and as sodium often aids in carrying phosphorus to the plant, it may thus render an indirect service.

It has indeed been suggested by Goodale [4] that sodium

[1] Ber. deut. bot. Gesell., *12* (1894), Gen. Vers., 114; quoted from Copeland.

[2] Bot. Gazette, *24* (1897), 411.

[3] The Physiology of Plants (translated by Ewart) (1900), *1*, 141.

[4] Physiological Botany (1885), 255.

may be substituted for a portion of the potassium required by the plant.

Owing to the large quantities of sodium in certain plants, A. Mayer thinks that it may perhaps be essential or at least serviceable to them.

FIG. 61. — ONIONS.

With full ration of common salt. Fertilized liberally with nitrogen and phosphoric acid and limed. In these respects like Figs. 62 and 63.

Attention has also been called by Mayer to the free movement of the salts of sodium within the plant, and he suggests that soda may just as well combine with organic acids in the plant as to have this service performed by some other base, and yet this would be without necessary

physiological significance. In this connection an experiment by Mercadante is of interest, for upon growing species of *Oxalis* and *Rumex*, without potassium, neither fruit nor flower formed, and but one-eighth the normal amount of acid was present. The oxalic and tartaric acids produced were found combined with lime, and but little starch or sugar was formed.

Under normal conditions, therefore, some of the organic acids, formed during the synthesis of the proteins, are found combined with potassium. This suggests that not only potassium, but also sodium, if there is a partial lack of the former, may perform a highly useful function as a neutralizer of organic acids, and, as Mayer has suggested, it may act as a soluble conveyor of at least oxalic acid to other parts of the plant, where by contact with lime the acid is precipitated as insoluble calcium oxalate. As a result the acid is prevented from reaching toxic proportions in certain vital parts of the plant.

It was held by Salm-Horstmar [1] as early as 1856 that sodium was essential to wheat and oats, in connection with the perfection of the seed.

From water-culture experiments with Indian corn, Stohmann [2] concluded that sodium was essential to its perfect development. It has been suggested by Müntz and Girard that if sodium is essential, the mangel wurzel is a plant most likely to require it. Sodium is mentioned also by Aikman, Johnson, and others, as possibly essential to plants; but if so only in very minute quantities.

496. Results by Jordan and Genter. — It was concluded by Jordan and Genter [3] that "soda cannot re-

[1] Versuche und Resultate über die Nahrung d. Pflanze, 12, 27, 29, and 36.

[2] Flora (1890), 207–261.

[3] Bul. 192, N. Y. (Geneva) Agr. Expt. Sta., December, 1900.

place potash as an active agent in the development of plant life," or, in other words, that it could not replace it in function though taking the place of some of it in the quantity found within the plant.

497. Soda in connection with diastatic action. — An interesting suggestion as to a possible independent physiological function of soda in plants has been made by Suzuki [1] in which he recalls the work of Chittenden, showing that the efficiency of vegetable diastase is heightened by small quantities of sodium chlorid (0.24 per cent). The same has been shown by Wachsmann [2] to be the case with animal diastase; furthermore it has been observed by A. Mayer that a 1 per cent solution of potassium chlorid not only retarded diastatic action, but that smaller amounts exerted no decisive effect. In consequence he concludes that sodium chlorid may act indirectly, in conjunction with the diastase, in the transportation of starch to the growing tips of plants.

498. Atterberg's experiments with soda. — An experiment is on record by Atterberg [3] in which plants were grown in quartz sand in which, in one series, calcium salts, and in another, sodium salts, were substituted for a part of the potassium, with the result that the yields fell off in the former case far more than in the latter. It has, however, been learned by correspondence that it was ascertained later that the particular lot of sand which was used in the experiments contained surprisingly large quantities of sodium chlorid, and hence it may also have contained some potassium salts capable of being liberated by sodium salts in a greater degree than by the action of lime. This,

[1] Bul. Col. of Agr., Tokyo, Imp. Univ., *6* (1905), No. 4, 408.
[2] Pflüger's Archiv, *91* (1902), 191.
[3] Deut. landw. Presse (1891), 1035.

therefore, throws some doubt upon whether the benefit was a direct one or was wholly or in part indirect, by virtue of the liberation of potash. The following year Wagner and Dorsch [1] called attention to the manurial value of sodium salts, asserting that, in case potash was lacking, sodium was capable, in connection with certain plants, of

FIG. 62. — ONIONS WITH MURIATE OF POTASH.

Full ration of muriate of potash. Fertilized liberally with nitrogen and phosphoric acid, and limed. In these respects like Figs. 61 and 63.

increasing the crop as much as one-half. Still later Stahl-Schroeder published certain researches which seemed to him to contradict the idea that the sodium in the experiments by Atterberg and by Wagner and Dorsch had exerted a direct effect, but rather that it was indirect by virtue of the liberation of potassium.

499. The experiments at Bernburg. — In a series of

[1] Die Stickstoffdüngung d. landw. Pflanzen (1892), 227–242.

experiments by Hellriegel, Wilfarth, and others,[1] at Bernburg, Germany, made in quartz sand or in mixtures of sand and peat, extracted previously in order to remove practically all of the available potassium, it was found that there was an increase in crops of barley and oats, when a deficiency of potash in the manures was partially made up by additions of sodium salts. There were indications, nevertheless, that buckwheat, potatoes, and perhaps other crops may not be benefited by sodium compounds.

In discussing the work of Hellriegel and Wilfarth, Schneidewind [2] calls attention to the fact that they were able, by substituting some soda for a part of the potash in the fertilizers, to produce the same amounts of sugar and of total dry matter as with the use of more potash. The latter believed, nevertheless, that the good effect of soda, which he had also observed in connection with beets, was not due to physiological functions of the sodium salts, but to the fact that the solubility of the sodium nitrate, sodium phosphate, and sodium sulfate was greater than the solubility of the corresponding potassium salts; and that on this account the several plant foods when in combination with sodium were more available. This latter conclusion is, however, open to serious question in view of the fact that Hellriegel and Wilfarth worked in pots which were watered artificially in order that optimum amounts of water might at all times be maintained in the soil; furthermore, under ordinary soil conditions plants are known to make use, in a satisfactory manner, of the various potassium salts.

It has been pointed out by Hartwell and Pember [3]

[1] Arbeiten Deut. landw. Gesell., Hefts 34 and 38.

[2] Jour. f. Landw. (1898), 7, 8.

[3] An. Rpt., R. I. Agr. Expt. Sta., *21*, 249, 250.

that in the experiments by Hellriegel and Wilfarth, when sodium was added, more potassium was removed in the crop than otherwise; and, furthermore, that the increase in growth was no more than might have been expected from the extra potassium thus rendered available. It was assumed by the latter investigators that when the sodium salts were deficient in the soil-culture medium, some of the potash applied in the fertilizers was fixed by the silica or otherwise, in such form that all of it could not be readily secured by the plants, but that a part of the potassium thus fixed was rendered available to a greater degree upon the addition of sodium salts.

500. The Rhode Island experiments. — It was on account of the many conflicting ideas as to the possible functional benefit of sodium salts that the matter has been studied exhaustively at the experiment station of the Rhode Island State College. At first, plants were grown in the field, in which case great benefit from common salt and from sodium carbonate resulted, when employed in connection with small applications respectively of muriate of potash and of potassium carbonate. In fact, even in cases where more than 300 pounds of muriate of potash, or its equivalent of potassium carbonate, were employed, the yields of mangel wurzels were doubled by sodium salts. In all cases heavy applications of organic nitrogen (chiefly in dried blood) and of available phosphates were made, in order to eliminate, in so far as possible, any effect of the sodium salts by way of rendering nitrogen and phosphoric acid available to the plants. In the course of this work many different kinds of plants were analyzed in order to determine the influence of the soda upon the composition of the mineral matter [1] and, in some cases,

[1] An. Rpt., R. I. Agr. Expt. Sta., *19*, 186–316.

upon the organic constituents of the plants. This work indicated that benefit from soda seemed to have resulted, in certain cases, which could not be readily explained upon the assumption that it was due to a greater liberation of potash. In order, however, to further remove doubt

FIG. 63. — ONIONS.

Full ration of common salt and full ration of muriate of potash. Fertilized liberally with nitrogen and phosphoric acid, and limed. In these respects like Figs. 61 and 62.

on this point, an extensive series of water-culture experiments was made at the Rhode Island station by Wheeler, Hartwell, and Pember,[1] and by Braezeale, under conditions where indirect manurial action was impossible. Precautions were also taken to eliminate the possibility of benefit from the sodium salts being due to a change in

[1] An. Rpt., R. I. Agr. Expt. Sta., *20* (1906–1907), 299–357; An. Rpt., *21* (1907–1908), 243–285.

the relation of the nutrients, to the chemical reaction, to the concentration of the solution, or to other similar effects, rather than to some physiological function of the sodium salt. As a result it appeared that though possibly unable to wholly replace potash in any one function, or at least in all of its functions, in connection with the growth of certain plants, sodium may and often does perform some part of one or more of the important functions of potassium, and thus increase the amount of dry matter which the plant can produce.

501. The practical significance of soda in agriculture. — The most practical feature connected with the utilization of sodium salts is to use for the growing of mangels, radishes, turnips, and such other crops as can make good use of them, fertilizers like nitrate of soda and kainit, which furnish nitrogen and potash; and at the same time, without added cost, supply soda. The soda, in such cases, serves as an insurance against a possible shortage of potash and may materially add to the yields.

CHAPTER XXIV

IRON AND MANGANESE

The importance of iron to plants has long been known, and now new interest attaches to manganese.

502. Iron in its relation to plant growth. — Experiments have shown that a lack of iron in plants causes pathological chlorosis, and it is believed that it may affect the protoplasmic structure in which the chlorophyl is deposited. It is therefore vital to the higher plants.

The necessity of iron may be readily shown by growing Indian corn or other plants for some time in a nutritive solution, which is complete excepting for the omission of iron. After having reached an advanced stage of chlorosis, the condition can still be remedied in a very short time by the addition of ferric chlorid to the nutrient solution.

Sufficient iron is present in practically all soils to meet the ordinary needs of plants. It has, nevertheless, been asserted that certain soils of northern Michigan are so deficient in this element that the plants grown upon them do not furnish sufficient iron to the cattle of the region to permit of their being brought successfully to maturity. It is stated that this can be accomplished, nevertheless, if they are supplied with fodder brought from elsewhere, or if they are removed after a time to some other section of the state.

Certain salts of iron may be reduced to lower oxid combinations under anaërobic soil conditions, or the lower

combinations may be oxidized upon draining the land or in times of drought. This latter change accounts for the frequent transformation from a bluish to a reddish brown tint observed in soils when, upon their exposure to the air, iron carbonate is oxidized to hydrous sesquioxid of iron. Where, as in muck and peat soils, the conditions are at times only partially favorable to oxidation, toxic organic compounds of the lower oxid of iron are said to result. In better aërated bogs, also, toxic iron protosulfate ($FeSO_4$ + Aq.) may be formed by the oxidation of iron sulfid (FeS_2), provided the latter is present in the sands or gravels frequently used as a covering for the surface. In the latter case the toxicity can be counteracted by liming, whereupon the iron salt is broken up to form gypsum, and the iron is further oxidized. Similar, but usually less striking, effects may also be noted in wet uplands.

503. Manganese in plants and soils. — It has been said that the existence of manganese in plants was first pointed out by Scheele, who found it in the ash of wild anise and of certain kinds of woods. It was later noted by Herapoth in the ash of the radish, beet, and carrot and by Salm-Horstmar in oats.

In 1872 Le Clerc recognized manganese as almost universally present in soils and plants, although present in the former usually in quantities much below 1 per cent.

504. Manganese as a fertilizer. — It was found by Giglioli that manganese dioxid increased the yields of both corn and wheat.

Experiments by Fukutome[1] have shown that the employment of ferrous sulfate, in conjunction with manganese chlorid, was very helpful to flax, whereas either employed without the other had but little effect. In experiments by

[1] Bul. Col. of Agr., Tokyo, *6* (1904–1905), 137.

Garola, also with flax, it was found that the employment of salts of manganese in the manures not only increased the growth, but also the assimilation of nitrates, phosphorus, potassium, calcium, and other ingredients.

Soils that were "oat-sick" were restored by Sjollema and Hudig to a normal condition upon the employment of manganese sulfate.

The amounts of manganese which may be safely and often profitably applied per acre, range, according to various experimenters, from nine to thirty-six pounds per acre. It is recommended that the salts be pulverized and mixed with the chemical fertilizers which are employed, or that they be mixed with the stable manure before it is applied to the land.

505. The manganese in Hawaiian soils. — Recent examinations of certain black Hawaiian soils have shown that they contain from about 4 per cent to nearly 10 per cent of manganese oxid (Mn_3O_4), whereas the red soils of Hawaii show a range of from only 0.15 to 0.37 per cent.

506. Plants unlike in endurance of manganese. — It appears that agricultural plants are very unlike in their relation to manganese, for the quantity present in the black Hawaiian soils, although not enough to interfere with the successful growth of sugar cane, is so toxic to pineapples that the plants often fail to bear fruit. Likewise Aso[1] found rice more resistant than either barley or wheat to salts of manganese, and he has also shown that its ill effects are worse in cold than in warm weather.

507. Variations in the manganese content of plants. — Manganese is very commonly present in the ash of plants, and Kelley[2] reports that the content of Mn_3O_4 found

[1] Bul. Col. of Agr., Tokyo, Imp. Univ., *5*, 177–185.

[2] The Jour. of Ind. and Eng. Chem., *1* (1909), 536.

in the ash of pineapple leaves varied from 1.65 to 2.12 per cent, which he considers low in view of the high manganese content of the soil upon which they were grown. In the ash of the bark and leaves of the Norway spruce, Schroeder found 35.5 and 41.2 per cent, respectively, of Mn_3O_4. The fact that so little manganese is found in some plants has led to the suggestion that possibly at certain stages of the growth of the plant it may pass back into the soil through the roots, or that it may be excreted from the aërial portions of the plants, as has been shown to be the case with certain other mineral plant constituents.

508. The effect of manganese on enzymes. — It was shown by Bertrand [1] many years ago that much manganese is present in the ash of oxidizing enzymes and that certain soluble salts of manganese increase the power to carry oxygen. In consequence, he suggested its practical trial by making application of it to the soil.

The beneficial results from the use of manganese are supported also by the experiments of Loew and Sawa. The latter investigators found that manganese sulfate, in moderate quantities, was toxic to barley. It exerted a bleaching action upon the chlorophyl, and increased the intensity of the oxidase and peroxidase reactions.

509. Manganese increases many crops. — When used in very dilute solutions, manganese sulfate was found by Loew and Sawa to promote the development of the plants.[2] The same was found by Aso to be true of rice; and Nagaoka [3] reports an increase of 37 per cent in rice, upon the application of 13.7 pounds of manganese sulfate per acre (77 kilos per hectare). A similar result is reported by

[1] Compt. rend. (Paris), *124*, 1032.
[2] Bul. Col. Agr., Tokyo, Imp. Univ., *5*, 172.
[3] *Ibid.*, *6*, No. 1.

Voelcker from Woburn (England) in experiments with wheat and other crops. In experiments by Sutherst [1] it was found that small amounts of manganese compounds, including the dioxid, were helpful to maize, yet he states that Salamone found large amounts injurious.

It has been shown by A. Anduard and P. Anduard that the employment of manganese increased the yields of wheat and of kidney beans, but lessened slightly the yields of carrots and of potatoes.

510. Roots change the oxidation of manganese. — In view of the alleged oxidizing power of plant roots, which it is asserted is even stimulated by salts of manganese, it is of interest to note that Kelley found the soil darker immediately about the roots of unhealthy pineapple plants than elsewhere, and that Aso discovered manganese dioxid adhering to the roots of wheat grown in solutions containing manganese sulfate, thus showing that the roots effect a change in the oxidation of the manganese. It is, however, claimed by Schreiner and Sullivan [2] that the beneficial effect of manganese is due to its promoting oxidation; they assert, however, that "the relation between oxidation and catalysis is not as clear as it should be, even in the plant where it has been extensively studied." It is evident in any event that manganese, if employed for its alleged "catalytic," "stimulating," or "oxidizing" effect, must be used very cautiously, especially if the degree of sensitiveness of the particular plant under experiment is not known at the outset.

511. Manganese may aid chlorophyl development. — In growing plants by way of water-culture, it has been found that if iron is slightly deficient, the addition of a

[1] The Transvaal Agr. Jour., *6*, No. 23.

[2] Bureau of Soils, Bul. 73, U. S. Dept. of Agr. (1910).

soluble manganese salt causes chlorophyl development and the renewed vigor that would be expected in such a case; yet, as was pointed out by Sachs [1] and later by Loew and Sawa, iron cannot be fully replaced by manganese in the production of chlorophyl.

A very full review of the experiments thus far conducted with manganese is given by Giglioli and Rousset,[2] and brief reference to much of the work is also made by Schreiner and Sullivan (*l. c.*) and others.

[1] Hoffmeister, Handbuch Phys. Botanik, *4* (1865), 144; cited from Schreiner and Sullivan.

[2] Ann. Sci. Agron., *2* (1909), 81.

CHAPTER XXV

CHLORIN, SULFUR, SILICA, CARBON DISULFID, TOLUENE, AND OTHER MISCELLANEOUS SUBSTANCES

Many miscellaneous substances including iodin, bromin, boron, lithium, and others have been tested as to their influence on plant growth, but only the more important of these are considered in this chapter.

512. Chlorin. — Whereas there have been some instances in which chlorin has seemed to be slightly beneficial to plant growth, especially in connection with buckwheat, potatoes, and possibly other plants, through some indirect action not definitely determined, it is nevertheless considered as a non-essential element. For this reason it is not classed as a plant food.

513. Sulfur. — Sulfur is essential to plant growth, and it is required in considerable amounts in the formation of certain essential oils, like those of the horseradish, cress, and for the proteins, which are present in all plants. It is, nevertheless, one of the elements supposed to be seldom, if ever, so deficient in soils as to require that it be supplied artificially. This is more especially the case in regions where the extended use of ready-mixed commercial fertilizers is common, since they usually contain considerable quantities of gypsum as one of the ingredients, not only of ordinary superphosphates, but also of certain of the German potash salts. Sulfur is also added to soils in potassium sulfate, in the low and high grade sulfates of

potash, and likewise in the protein compounds of nitrogenous organic fertilizing materials.

514. Sulfur may become depleted in soils. — It has been shown by Hart and Peterson that where farm-yard manure is applied to soils regularly and in reasonable quantities, the original quantity of sulfur in the soil is maintained or even increased. Soils, on the contrary, which have been cropped for from fifty to sixty years, and which have received but little manuring, were found to have lost 40 per cent of their original sulfur, as indicated by comparisons with similar virgin soils.

It has been further pointed out by Hart and Peterson that many crops remove sulfur from the soil in much greater quantities than those usually given in the tables of analyses of farm crops. This fact, however, may merely signify that a great excess of sulfur is present in the soil in assimilable form, and hence the results may serve as a more effective argument against its lack than for the necessity of its application.

515. The relation of sulfur and phosphorus in plants and soils. — The fact has also been pointed out by Hart and Peterson that the amount of sulfur trioxid represented in average crops of the grain and straw of cereals is about two-thirds as great as the amount of phosphoric acid which these crops remove; that in mixed meadow hay the quantities of the two are about equal; and in certain legumes the amount of sulfur trioxid represented may approach, and in alfalfa even exceed, the amount of the phosphoric acid.

An average crop of cabbage is said to remove from the soil the equivalent of 100 pounds per acre of sulfur trioxid, and in normal soils the amount in an acre-foot of soil was found by the method of fusion with sodium peroxid to be only from 1000 to 3000 pounds.

The annual addition to the soil of sulfur trioxid in the rainfall, as estimated by Hart and Peterson, for Madison, Wisconsin, is said to be from 15 to 20 pounds per acre, whereas the estimated losses by leaching, based upon the yearly drainage from the Rothamsted (England) experimental fields, are assumed to be about 50 pounds per annum.

516. Need of sulfur may need investigating. — In view of the preceding, and other facts, and of the attention called by Bogdanov,[1] as well as by Dymond, Hughes, and Dupe [2] to the possible importance of the sulfur question, Hart and Peterson believe that the possible need of an artificial supply of sulfur should be given due consideration in connection with future researches involving soils and fertilizers.

517. Silica in plants. — Silica is an important constituent of the ash of the grasses and rushes and also of many other plants. The ashes of some clovers, and of the straws of cereals, have been found to contain from 40 to 70 per cent of silica. In fact, this plant silica, by virtue of its unusual solubility, may have some heretofore unconsidered value in the soil, in connection with green manuring and with the use of stable manure and straw, by way of aiding in the formation of zeolitic double salts of lime, magnesia, and the alkalies, by which the absorptive capacity of light soils may be advantageously increased.

518. Suggested functions in plants. — Silica has been supposed to serve as a protection and support in the cell walls, although not considered absolutely essential to plant growth.

[1] Abs. E. S. R., *11*, 723.
[2] Jour. Agr. Sci., England, *1* (1905), 217.

It has been asserted by Wolff that silica favors the migration of phosphoric acid from maturing stems and leaves to the seeds which are in process of development; for he secured a larger number of perfect grains in its presence than in its absence. Nevertheless, four generations of maize were grown by Jodin without silica, other than that derived from the dust of the air and from the vessels used in the experiment, but yet without apparent ill effect upon the plants. From what is now being learned about individual plant peculiarities, it would, however, be unwise to conclude from experiments with maize as to the needs of all other higher plants.

519. Silica may replace other ingredients in the "luxury" consumption. — In experiments with oat plants Wolff determined, in the presence of an abundance of all of the other essential elements, the minimum of each which was necessary, but found nevertheless that he could not grow plants containing only these minima of all of them. In other words, there seems to be required a certain excess of mineral matter beyond such calculated minima, a part of which "luxury" need may be supplied by silica very much as sodium seems to answer a part of the general need for a soluble base when potash is present only to the extent of that minimum vital to plant growth.

520. Silica deposition checks sap diffusion. — It has been suggested by Ritthausen that silica performs a useful function through its well-regulated and gradual deposition as a gelantinous mass in the walls of cells, by which the diffusion of sap is gradually suspended, especially in the lower leaves which gradually become unnecessary and ineffective. By this process, the chief portion of the plant food contained in such leaves, together with all of the sap, is ultimately diverted to the building up of new shoots

and to parts of the plant which, in the later stages of growth, have become more important.

521. Carbon disulfid often increases crops. — It was pointed out by A. Girard in 1894, in connection with experiments extending over a number of years, that highly beneficial effects upon the growth of plants followed applications to the soil of carbon disulfid, which had been used at the rate of 2904 pounds[1] per acre for the destruction of beet nematodes. The beet crop was ruined by the treatment, but the following year the wheat crop on the treated area was much better than elsewhere. Subsequent experiments, in which carbon disulfid was used at the same rate, resulted in a gain of from 15 to 46 per cent in the yield of wheat grain, and of from 21 to 80 per cent in wheat straw. The yield of potatoes was similarly increased by from 5 to 38 per cent, and that of beets from 18 to 29 per cent. The yield of clover was also increased by from 67 to 119 per cent. In the case of oats there was an increase in 1891 of 9 per cent in grain and of 30 per cent in straw. At Joinville, in 1892, oats showed a gain, from its use, of 100 per cent in grain and of 60 per cent in straw.

522. Reasons suggested for the benefit to soils from using carbon disulfid. — For a long time much doubt existed as to the cause of the benefit which resulted from the use of the carbon disulfid. Among the suggestions offered in explanation was one to the effect that the material might have acted as a "stimulant," also that it might have aided by destroying certain "injurious subterranean insects" or "cryptogamic organisms," which might otherwise exert an injurious effect upon the roots of plants. This latter view was held by C. Oberlin,[2] an

[1] Also E. S. R., *6* (1894–1895), 564, 565.

[2] *Ibid.*, 565.

Alsatian viticulturist who had made similar observations on vegetables, cereals, and forage crops.

It was suggested by Milton Whitney that the effect of the carbon disulfid might be due to an alteration of the physical character of the soil.

It had already been established by Warrington and was supported later by J. Perraud [1] that carbon disulfid checks excessive nitrification, but it was supposed that this was offset by benefit in other directions.

Subsequent investigations made by P. Wagner led him to conclude that the preservative action of carbon disulfid on stable manure, and its beneficial action on soils, were probably due to its destruction of denitrifying organisms.[2]

523. Treatment of soils with carbon disulfid costly. — The expense of the disulfid treatment at the time of the earlier experiments was very great. In fact, at the French price, $3\frac{1}{2}$ cents per pound, it cost $96 per acre, and at the prevailing American prices, due to the high tariff and other causes, the cost of treatment was $290 per acre. The use of such costly amounts of carbon disulfid simply for soil improvement was obviously not economical, but the experiments justified the belief that if but 175 to 290 pounds per acre were employed, or such quantities as were customarily applied in vineyards, that some benefit would result aside from the mere destruction of the phylloxera.

524. Carbon disulfid cures certain vetch clover and alfalfa "sick" soils. — Certain experiments by Oberlin [3] have shown great benefit from the previous employment of carbon disulfid. He found that a soil made "alfalfa

[1] Abs. E. S. R., *6* (1894–1905), 565.
[2] L'Engrais, *10* (1895), No. 18, 423; Abs. E. S. R., *7*, 25.
[3] Jour. Agr. Prat., *59* (1895), 459–464, 499–503, 535–540.

sick " by the continuous growth of the crop for six years could be effectually cured by it, at least for a time. Similar results were secured also with hairy vetch and crimson clover. It is of interest to note that, among other queries, Oberlin raised the question if the treatment destroyed all soil organisms or only certain classes of them.

525. Carbon disulfid not the only unusual compound to benefit soils. — It is impossible here to follow all of the developments in connection with sterilization by the heating of soils, likewise the use of carbon disulfid and all of the many other soil disinfectants, catalyzers, stimulants, indirect fertilizers, or whatever they may have been termed. Among these may be prominently mentioned toluene, tricresol, chloroform, zinc sulfate, and potassium permanganate. Most, or at least many of these compounds are too costly to permit of their general extensive application, even though they may be highly beneficial in certain special cases, and zinc compounds and certain other substances may, by their accumulation in the soil, become ultimately toxic.

526. Disinfectants, like heating, destroy soil amebe. — Recently added interest has been lent to the subject of disinfecting soils by the observations of Loew [1] to the effect that soil " infusoria, flagellatæ, and amœbe devour great numbers of microbes." This was soon followed by the address of A. D. Hall [2] delivered at Sheffield, England, in 1910, in which he called attention to the fact that Russell and Hutchinson of the Rothamsted laboratory had found that soils which had been subjected to sterilization by chemical treatment were found to contain exceptional amounts of ammonia, sufficient, in fact, to account for their

[1] Science, *31* (1910), 988.
[2] *Ibid.*, *32* (1910), 363.

subsequent increased fertility. It was further pointed out that the sterilization was not complete, yet at the outset it greatly lessened the number of bacteria. This was, however, but temporary, for after the soil was watered and allowed to stand, it was discovered that they had increased far in excess of the normal numbers. A given Rothamsted soil, for example, containing normally seven million bacteria per gram, contained but four hundred after heating; yet a few days later the number present amounted to six millions and later reached forty millions per gram of soil.

Toluene treatment. — Treatment of the soil with toluene resulted similarly, and the increase in ammonia in the soil was explained by the rapid multiplication of bacteria, a conclusion suggested by the fact that their increase was coincident with this gain. The nitrifying bacteria were eliminated by the treatment, and those remaining were of the ammonifying group. This work led to the idea that the treatment had destroyed something which had previously limited the bacterial development, and upon further investigation it was found to have been the protozoa which fed upon the living bacteria. With the destruction of these protozoa the ammonification of the organic matter in the soil progressed rapidly. The protozoa probably concerned in the destruction of the bacteria were found to be amebe and ciliates, for they were killed by partial sterilization.[1]

527. Destruction of soil protozoa may explain benefit from soil "firing" and deep plowing. — The preceding observations afford a probable explanation of a part of the beneficial results following the old practice of "firing" or burning soils; and also the practice of the Bombay

[1] Russell, E. J., Science, *36* (1913), 520.

tribes, who were accustomed to burn rubbish with as much of the surface soil as possible before sowing their seed; for such treatment would be highly destructive to protozoan life.

It has since been claimed by Loew that the protozoa can probably only exist on or near the surface layers of such soils as are very compact, for the reason that the bacteria would be likely to render the store of air at the lower levels unfit for the respiration of the many protozoa. Nevertheless, in the Rothamsted soil, amebe are found at considerable depths. It may nevertheless be true that they exist chiefly in the surface layers of other soils. If this be true, the suggestion of Loew's might explain some part of the benefit sometimes resulting from deep plowing, as compared with a shallow working of the soil by harrowing, since the protozoa would be transferred thereby to the lower levels and would possibly be largely destroyed, thus giving a better chance for the development of the beneficial bacteria and for the rapid accumulation of an abundance of quickly available nitrogen.

528. The general applicability of soil disinfection doubted by Loew. — Notwithstanding that Loew admits the possible correctness of the conclusion of the Rothamsted investigators, and the possibility of the usefulness of such treatment in special cases, he does not think that it will admit of general application; furthermore, he points out the chance for the increase of possibly harmful as well as of beneficial organisms, as a result of sterilization. It is asserted, however, by Russell[1] that, "The improvement in the soil is permanent; the high bacterial numbers being kept up even for 200 days or more."

[1] Science, *37* (1913), 519.

529. The chlorid of lime treatment of soil tried by Loew. — In connection with the study of a soil which had become sick for lilies, Loew made a trial of carbon disulfid, tricresol, potassium permanganate, and chlorid of lime. It was found that beneficial results followed the use of all of these substances, but that chlorid of lime was the most effective and the least costly of them all. Since this is perhaps the first time that chlorid of lime (bleaching powder) has ever been used for this particular purpose, it may be stated that to an area 1.5 meters long and 1 meter wide, 100 grams of chlorid of lime were applied, dissolved in 5 liters of water. A part of the solution was spread over the surface, and the remainder was poured into holes made in the soil.

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